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INTRODUCTION TO MODERN PHYSICS

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BY

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To My Wife

PREFACE

For several years, the author has given at Cornell University, and, occasionally, in summer sessions, elsewhere, a course of lectures under the title "Introduction to Modern Physical Theories." These lectures have been adapted, as far as possible, to meet the needs of two groups of students: (1) those special students in physics who, before entering the specialized graduate courses, desire a survey of the origin and development of modern physics in order the better to understand the interrelations of the more advanced courses; and (2) those students who, pursuing either academic or professional curricula and having had the usual elementary undergraduate courses in physics, wish a further bird's-eye view of the whole subject. This book is based upon these lectures and has been prepared, although rather reluctantly, as a result of the importunities of former students and other friends.

The purpose of this book is, frankly, pedagogical. The author has attempted to present such a discussion of the origin, development, and present status of *some* of the more important concepts of physics, *classical as well as modern*, as will give to the student a correct perspective of the growth and present trend of physics as a whole. Such a perspective is a necessary basis—so the author, at least, believes—for a more intensive study of any of the various subdivisions of the subject. While for the student whose interests are cultural, or who is to enter any of the professions directly or indirectly related to physics, such as engineering, chemistry, astronomy, or mathematics, an account of modern physics which gives the *origin* of current theories is likely to be quite as interesting and valuable as is a categorical statement of the theories themselves. Indeed, in *all* branches of human knowledge the "why" is an absolutely indispensable accompaniment to the "what." "Why?" is the proverbial question of childhood. "Why?" inquires the *thoughtful* (!) student in classroom or lecture hall. "Why?" demands the venerable scientist when listening to an exposition of views held

by a colleague. Accordingly, if this book seems to lay somewhat greater emphasis on matters which are frequently regarded as historical, or, if here and there a classical experiment is described in greater detail than is customary, it is with a desire to recognize the importance of "why."

If one were to attempt to answer all of the "why's" raised by an intelligent auditor in answer to a categorical statement, such as, "The atom of oxygen is composed of eight electrons surrounding a nucleus containing four alpha particles," one would have to expound a large part of physical science from Copernicus to Rutherford and Bohr. To attempt a statement of even the more important concepts, hypotheses, and laws of modern physics and of their origin and development would be an encyclopedic task which, at least in so far as concerns the aim of this book, would fall of its own weight. Accordingly, it has been necessary to select those parts of the subject which best serve our purpose. This selection, as well as the method of presentation, has been based upon the experience gained in giving the above-mentioned lectures to numerous groups of students. Many very important developments, particularly the more recent ones, either have been omitted entirely or have been given only a passing comment. And even in those parts of the subject which have been discussed, there has been no attempt to bring the discussion strictly up to date. Indeed, with the present rapid growth of physics, it would be quite impossible for any *book*, even a special treatise, to be strictly up to date. Happily, for our purpose, up-to-dateness is not an imperative requisite, since it is assumed that the student who wishes the *latest* knowledge will consult the current periodicals.

In this connection, it should be emphasized that this book is an *introduction* to modern physical theories and is intended neither as a compendium of information nor as a critical account of any of the subjects discussed. In preparing the manuscript, the author has consulted freely the many very excellent texts which deal with the various special topics. Save for here and there a very minor item, or an occasional novelty in presentation, the book makes no claim to originality, except, perhaps, as regards the viewpoint from which some parts have been written.

It is assumed that the student is familiar with the elementary principles of calculus, for no account of modern physics can dispense with at least a limited amount of mathematical dis-

cussion, if for no other reason than to emphasize the fact that, in the progress of physics, *theory* and *experiment* have gone hand in hand. Partly, however, for the sake of brevity and partly in the attempt always to keep the underlying physical principles in the foreground, numerous "short cuts" and simplifications, some of them perhaps rather questionable from a precise standpoint, have been introduced. These elisions should cause no confusion.

The student who, in his educational career, has reached the point where he can, with profit, pursue a course based on such a book as this, has passed beyond the stage where he assimilates only the material presented in lecture or class and has come to regard a "course" as a channel to guide his own independent studies, branching out from the "course" in such directions as his fancy or interests may lead him. It is hoped that students reading this book will do likewise. Deliberately, the author has not given a collected bibliography at the end of each chapter, or a list of problems and suggested topics for study. Rather, references, in most cases to original sources, have been given at appropriate points in the text, and it is hoped that, starting from these references, the student will prepare his own bibliography of such parts of the subject as appeal to him. The advantage to the student of such a procedure is obvious. Quite apart from the value of the experience gained in making contact with, and in studying, the literature of any subject, the reading of *first-hand* accounts of at least some of the more important developments will give the student a better understanding of the subject than can, in general, be gained by textbook study only. Accordingly, he will find here and there throughout this book suggestions of important articles which should be read in the original. Likewise, in many places the discussion has, of necessity, been brief, and the student is referred to special treatises for further details. Various supplementary questions and problems will also arise at numerous points as the student reads the text.

There is no more fascinating story than an account of the development of physical science as a whole. (*Any* scientist would probably make the same statement about *his own* science!) Such a study leads to certain broad generalizations which are of outstanding importance in evaluating current theories and concepts. For example, one finds that, taken by and large, the evolution of physics has been characterized by *continuity*. That

is to say: With few exceptions, the ideas, concepts, and laws of physics have evolved *gradually;* only here and there do we find *outstanding* discontinuities. The discovery of photoelectricity, of X-rays, and of radioactivity represent such discontinuities and are correctly designated "discoveries." But we must use "discover" in a quite different sense when we say that J. J. Thomson "discovered" the electron. The history of the electron goes back at least to Faraday. Thomson's experiments are all the more brilliant because he succeeded in demonstrating, by direct experiment, the existence of something, evidence concerning which had been previously *indirect.* Then, there are the respective roles played by qualitative and by quantitative work. Numerous important discoveries have been made "by investigating the next decimal place." Witness the discovery of argon. And ever since Kepler proved that the orbits of the planets are ellipses, relations expressible in *quantitative* form have carried greater weight than those which could be stated only qualitatively. For example, Rumford's experiments on the production of heat by mechanical means were suggestive. But Joule's measurement of the mechanical equivalent of heat was *convincing.* If, directly, or indirectly by inference, the author has succeeded here and there in the text in pointing out such generalizations as these, one more object which he has had in mind will have been accomplished.

The author wishes to take this occasion to acknowledge his obligations to those who have aided in the preparation of this book: to his wife, for assistance in preparing the manuscript and in proof reading; and to his many students, whose generous approbation of the lecture courses upon which the book is based has, in a large part, inspired its preparation. He is particularly indebted to Dr. J. A. Becker, of the Bell Telephone Laboratories, Inc., for his invaluable aid in reading the manuscript, pointing out numerous errors, and suggesting important improvements.

F. K. RICHTMYER.

ITHACA, N. Y.
July, 1928

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INTRODUCTION TO MODERN PHYSICS

INTRODUCTION

1. The term "modern physics," taken literally, means, of course, the *sum total* of knowledge included under the head of present-day physics. But by "modern physics," many writers and speakers frequently mean that part of present-day physics which has been developed during the past twenty-five or thirty years; in contradistinction to "classical physics," by which is meant the sum total of physics as it was known in, say, 1890. The justification for the latter use of the term is to be found partly in the fact that advances since 1890 have been very great indeed and partly in the fact that some of these advances have brought into question, or are in direct contradiction to, many of the theories which, in 1890, were thought to be firmly and finally established. For example, few, if any, physicists in 1890 questioned the wave theory of light. Its triumph over the old corpuscular theory was thought to be final and complete, particularly after the brilliant experiments of Hertz, in 1887, which demonstrated, beyond doubt, the fundamental soundness of Maxwell's Electromagnetic Theory of Light.

2. And yet, by an irony of fate which makes the story of modern physics full of the most interesting and dramatic situations, these very experiments of Hertz brought to light a new phenomenon—the photoelectric effect—which, together with a series of discoveries[1] coming in rapid succession in the single decade, 1887–1897, was the beginning of the development of the now famous quantum theory. This theory is, in many of its aspects, diametrically opposed to the wave theory of light. Indeed, the reconciliation of these two theories, each based on incontrovertable experimental evidence, may be said to be one of the two great problems of modern physics; the other problem being that of the structure of matter.

[1] Namely, X-rays in 1895; radioactivity in 1896; the electron in 1897.

3. It shall be the purpose of the following pages to give a brief outline of the origin, development, and, in so far as may be possible in this rapidly developing subject, the present status of these two problems.

4. But a history of the United States cannot begin abruptly with July 4, 1776. In like manner, if we would understand the full meaning of the growth of physics since, say, 1890, we must have clearly in mind at least the main events in the development of the subject up to that time. Accordingly, we shall begin our study by a brief account of the history of physics up to a half-century ago.

5. In presenting this brief historical survey, however, the author has in mind another purpose, toward which he hopes the reader will be, ultimately at least, sympathetic. Modern scientists have, with few exceptions, grossly neglected to cultivate the history of their respective sciences. How many physicists can answer the questions: When was the law of the conservation of energy first enunciated? Who was Count Rumford? Did the concept of universal gravitation spring full-grown from the head of that genius Newton? Indeed, when did Newton live?

Just as any good American should know the essential outline of the history of his country, so any good physicist should know the principal facts in the history of physics. For in that history, in the lives of those men whose labors have given us our subject, and in the part which physics has played in moulding human thought and in contributing to modern civilization, the student will find a story which is as full of human interest and inspiration as is any subject of the curriculum.

What can be more inspiring than the life of Michael Faraday and his whole-souled devotion to his work? Which have had a greater effect on present-day civilization: the victories of Napoleon or the electrons of J. J. Thomson? Was Roentgen when he discovered X-rays seeking a new tool to help surgeons set broken bones?

The physicist owes it to his science to possess such a knowledge of the history of physics as gives *him* a correct perspective of the development and present-day importance of the subject and, in turn, enables him to acquaint his lay contemporaries with these essential facts. If there *is* apathy on the part of the public toward physics, the physicist himself is largely at fault, since he is so absorbed in the interest of the present that he forgets the

importance of the past. He would find it much easier to justify to a popular audience the latest experiments on, say, the magnetic spectrum of electrons emitted from targets radiated by X-rays, if he prefaced his remarks by an account of the relation of Faraday's work to the modern dynamo.

It is hoped, therefore, that the student of these pages who proposes to follow physics as a profession, as well as the student whose interest is largely cultural, will extend the following all too brief historical sketch by independent study, particularly of biography.

6. In order to make it easier to keep the essential facts in mind, we may, somewhat arbitrarily, divide the history of physics into four periods.

The First Period extends from the earliest times up to about 1550 A.D., which date marks, approximately, the beginning of the experimental method. During this long era, there was, of course, substantial advance in the accumulation of the *facts* of physics as a result of the observation of natural phenomena, particularly by the Greeks, whose authority was almost unquestioned for many centuries. But the development of physical *theories* was rendered impossible, partly by the speculative, metaphysical nature of the reasoning employed, but more particularly by the almost complete absence of experiment to test the correctness of such theories as were proposed. The main characteristic of this period, therefore, is *the absence of experiment.*

7. The Second Period extends from 1550 to 1800 A.D. While numerous basic advances were made during this period—by such men as Gilbert, Galileo, Newton, Huyghens, Boyle, Benjamin Franklin—its most important characteristic is *the development and the firm establishment of the experimental method* as a means of scientific inquiry, as is well illustrated by Galileo's famous experiment (about 1590) of dropping two bodies of unequal weight from the leaning tower of Pisa, thereby proving *by experiment* the incorrectness of the assertion of Aristotle that the heavier body would fall more rapidly—an assertion which had been believed implicitly for nearly two thousand years.

It took two centuries after Galileo's experiment to overcome prejudice, dogma, and religious intolerance and to bring universal recognition, even among scientific men, to the basic principle that

> . . . *science can advance only so far as theories, themselves based upon experiment, are accepted or rejected according as they either agree with or are contrary to other experiments devised to check the theory.*

8. The THIRD PERIOD, 1800–1890, is characterized by the development of what is now called "classical physics." The experiments of Count Rumford (about 1798) led ultimately to our present kinetic theory of heat. The observations of Thomas Young (1802) and his proposal of the principle of interference (of two beams of light) resulted ultimately in the triumph of Huyghen's Wave Theory of Light over the corpuscular theory, as supported by Newton. And the researches of Faraday gave Maxwell the material for the crowning achievement of this period, namely, the electromagnetic theory.

So profound were these, and many other, developments that, by 1880, not a few physicists of note believed that all the important laws of physics had been discovered and that, henceforth, research would be concerned with clearing up minor problems and, particularly, with improvements of methods of measurement so as "to investigate the next decimal place." They could not have foreseen that the world of physics was on the eve of a series of epoch-making discoveries, destined, on the one hand, to stimulate research as never before and, on the other, to usher in an era of the application of physics to industry on a scale previously unknown.

9. The FOURTH PERIOD dates quite definitely from the discovery of the photoelectric effect, in 1887. In rapid succession, followed the discovery of X-rays, in 1895; of radioactivity, in 1896; of the electron, in 1897; and the beginning of the quantum theory, in 1900.

So varied and extensive have been the developments in both pure and applied physics from that time to the present that it is difficult to characterize this period by a single appelation. Hence, perhaps one may use the pleonasm "modern physics." Only the historian of a century hence can properly evaluate the growth of physics during the first part of the twentieth century. We, of the present, are too close to it to grasp its full significance.

10. It is, obviously, far beyond the scope of this book to give a detailed account of the history of physics during each of these four periods. Rather, the material chosen for discussion, particularly the biographical notes, is to be taken as representative. It should, also, be pointed out that so many of the advances in physics have come, either directly or indirectly, from astronomy, that frequent reference to the history of the latter subject will be made.

CHAPTER I

HISTORICAL SKETCH, FIRST PERIOD: EARLIEST TIMES TO 1550 A.D.

1. The Greeks.—It would be quite incorrect to say that the Greeks were entirely unacquainted with physical laws and facts. Relatively speaking, their contributions to the natural sciences were far less than to mathematics, literature, art, and metaphysics. But, in spite of their vague and misty philosophizing concerning natural phenomena, and in spite of their failure to test theory by experiment, the Greeks gave to the world much of the physics that was known up to 1400 A.D. And in their writings one finds, here and there, the germ of such fundamental modern principles as the conservation of matter, inertia, atomic theory, the finite velocity of light, and the like.

Certain of these ideas—for example, the heliocentric hypothesis of Aristarchus—doubtless led to further developments centuries later. Others—for example, the atomic hypothesis of Democritus—probably had little or no connection with the modern counterpart, largely on account of the speculative reasoning upon which the Greek theories were based.

2. Thales of Miletus (624–547 B.C.), according to the later writings of Aristotle, was acquainted with the attractive power of magnets and of rubbed amber. According to some authorities, he was able to predict eclipses, but others claim that he was rather the first to explain the cause of eclipses.[1] Apparently, the Chaldeans some 2,000 years B.C., had devised a rule-of-thumb method for predicting eclipses, on the basis of their discovery that, after a cycle of 18 years, eclipses repeat themselves in the same order, a little later in the year. Other discoveries and doctrines attributed to Thales[2] are the inclination of the ecliptic; the spherical shape of the earth; and the measurement of the angular diameter of the moon, as seen from the earth, as $\frac{1}{720}$ part of a whole circle. Aristotle credited Thales, however, with the doctrine that the earth was cylindrical in shape and rested on

[1] HEATH: "Aristarchus of Samos," pp. 12–23.

[2] ROSENBERGER: "Geschichte der Physik," vol. I, p. 6.

water; and, according to Heath (*loc. cit.*, pp. 21–23), there is reason to believe that the angular diameter of the moon had been measured by the Babylonians at least a thousand years before Thales' time.

3. Pythagoras (580–500 B.C.) was one of the greatest of the early Greek philosophers and the founder of the Pythagorean school. He seems to have been the first to hold that the earth was spherical, although the basis of his belief is not known. According to Heath, his arguments were probably based on "mathematico-esthetic" reasoning, since "the sphere is the most perfect of all figures." Pythagoras himself, and probably his immediate successors among the Pythagoreans, believed that the universe was spherical in shape, with the earth at its center, and that the sun, stars, and planets moved in independent circles around the earth as a center.

4. Philolaus, one of the later Pythagoreans and a contemporary of Socrates (470–399 B.C.), abandoned the geocentric hypothesis *and boldly reduced the earth to the status of a planet.* According to his system, the universe is spherical, finite in size, and has at its centre a "fire"[1] which contains the "governing principle" which directs the universe. The earth revolves around this central fire in a circle, once per day, always keeping its face outward, so that we never see the fire. Beyond the earth, revolving in similar but larger circles, come, in turn, the moon, the sun, the five planets (in the order Mercury, Venus, Mars, Jupiter, Saturn), and, last of all, the *sphere* containing the fixed stars. The period of revolution of the earth about this central "fire" is 1 day; that of the sun, about 365 days. (Day and night are thus accounted for.) Schiaparelli[2] gives the periods of revolution of these several bodies, as computed by Philolaus, and compares them with modern data as follows (the terrestrial day is the unit of time):

Planet	Period of revolution according to	
	Philolaus	Modern view
Saturn	10,752.75 days	10,759.22 days
Jupiter	4,301.10	4,332.58
Mars	693.71	686.98
Venus, Mercury, Sun	364.5	365.26
Moon	29.50	29.53

[1] This "fire" is *not* the sun, as some writers have apparently assumed.

[2] Quoted in HEATH'S "Aristarchus," p. 102.

5. Anaxagoras and Empedocles.—Almost contemporary with Philolaus were *Anaxagoras* (500–428 B.C.) and *Empedocles* (484–424 B.C.). According to Plato, Anaxagoras neglected his possessions in order to devote himself to science, and, indeed, he is said to have affirmed that his purpose on earth was "the investigation of the sun, moon, and heaven." Apparently, human nature, as well as human curiosity, has not changed for 2,500 years, for, to paraphrase a famous saying, the course of pure science has never run smoothly. Anaxagoras was accused of impiety because he taught that the sun was a red-hot stone and that the moon was simply earth. For holding this doctrine, he was banished from Athens—thereby becoming one of the first of a long line of martyrs of science.

Anaxagoras is credited with the almost epoch-making discovery that the moon does not shine by its own light but that "the sun places the brightness in the moon" and "the moon is eclipsed through the interposition of the earth." Also, "The sun is eclipsed at new moon through the interposition of the moon."[1]

Anaxagoras believed that the Milky Way is due to the shadow which the earth casts in the sky when the sun, in its revolution around the earth, is below the earth, thereby rendering visible the fainter stars—apparently, the principle involved being somewhat the same as that which makes it impossible to see the stars in the daytime. No explanation is offered as to why the moon is not, therefore, eclipsed when in the Milky Way. The theory was later refuted by Aristotle on essentially correct grounds, namely, that the shadow which the earth casts is a cone the apex of which does not reach the stars, since the sun is larger than the earth and is very distant, and the stars are still more distant.

To Anaxagoras is due the germ of the idea of the atomic hypothesis of Democritus, who lived in the next generation. Anaxagoras denied the contention of the earlier Greeks regarding the creation or destruction of matter and taught that these changes consist of combinations or separations of invisible, small particles (*spermata*) of matter. These particles themselves are unchangeable and imperishable and differ from each other in form, color, and taste—a doctrine which, qualitatively, foreshadows the law of the conservation of matter.

[1] HEATH: "Aristarchus," p. 78. Quotations cited from later Greek writers.

Empedocles reduced the elements in the theory of Anaxagoras to four—earth, water, air, and fire—through combinations and separations of which the All exists. He also held definite views concerning the phenomena of light. According to him, light is due to the emission by the luminous or visible body of small particles which enter the eye and which are then returned from the eye to the body, the two "streams" giving rise to the sense of form, color, etc.

Empedocles, according to Aristotle, proposed that light "takes time to travel from one point to another"—this theory, of course, being based on abstract speculation, rather than on observation or experiment. The theory was rejected by Aristotle, who stated that "though a movement of light might elude our observation within a short distance, that it should do so all the way from east to west is too much to assume."[1]

6. Democritus (460–370 B.C.) gave more definite, quantitative form to the atomic hypothesis of Anaxagoras by postulating that *the universe consists of empty space and an (almost) infinite number of indivisible and invisible particles* which differ from each other only in *form, position, and arrangement.* Bodies come into being, and vanish, only through combinations and separations of these atoms. This hypothesis Democritus regards as reasonable, for, he argues, the creation of matter is impossible, since *nothing* can come from *nothing* and, further, nothing which is can cease to exist. Aristotle[2] puts this argument for the indestructibility of matter in the naïve form: "If, then, some one of the things which are is constantly disappearing why has not the whole of what is been used up long ago and vanished away?" But he rejects the atomic hypothesis, which, on the basis of speculative reasoning alone, could not evolve beyond the point where Democritus left it. It was twenty-two centuries later, when Dalton, on the basis of *experimental evidence,* announced his law of multiple proportions, which, nourished by further experiments, rapidly grew into our present theory of the atomicity of matter.

With Empedocles, Democritus held that vision arises through the entrance into the eye of small particles—contrary to the then prevalent belief that vision resulted in something which

[1] Quoted in HEATH'S "Aristarchus," p. 93.

[2] "De Generatione et Corruptione," Book I, Chap. III; translated by H. H. Joachim. The Clarendon Press (1922).

"reached out" from the eye, just as the sense of touch involves reaching out our hands to grasp an object.

7. Plato (429–347 B.C.), although one of the greatest of the Greek philosophers, did not make contributions to physics such as are of interest in connection with the present discussion. Quite the opposite, however, is true of Aristotle, a pupil of Plato.

8. Aristotle (384–322 B.C.) contributed so much to all branches of knowledge—logic, rhetoric, ethics, metaphysics, psychology, natural science—that it is difficult to sift out that which is germane to a brief history of physics. Perhaps the most important single fact is the tremendous influence which, as a result of his intellectual brilliance and achievements in many branches of learning, he exerted for many succeeding centuries in *all* branches, physics included. Aristotle is justly entitled to fame for much of his work; but, viewed from our twentieth-century vantage point, not a little of his reasoning concerning the physical universe must be regarded as piffle. For example, in "De Generatione et Corruptione," he discusses the rather abstract question of the "coming-to-be" and the "passing-away" of things and argues for the indestructibility of matter by saying that (Book II, Chap. X) "it is far more reasonable (to assume) that *what is* should cause the coming-to-be of *what is not* than that *what is not* should cause the being of *what is*." Which is understandable. But then follows the curious argument: "Now that which is being moved *is*, but that which is coming to be *is not:* hence, also, motion is prior to coming-to-be . . . and we assert that motion causes *coming-to-be.*" But *coming-to-be* and *passing-away* are two processes contrary to one another. Therefore, says Aristotle, we must look for *two* motions, likewise contrary, as the cause of both *coming-to-be* and *passing-away*. Since these processes go on continuously, we must look for continuous motion. Only motion in a circle is continuous, and motion in an inclined circle has the necessary duality of opposing movements. Such a motion is that of the sun, which, as it approaches (spring), causes *coming-to-be* and, as it retreats (autumn), causes decay. The motion of the sun along the ecliptic is, therefore, the cause of generation and destruction.

And yet Aristotle frequently calls in observed facts to substantiate his speculation. For example, in "De Caelo" (Book II, Chap. XIV), after proving, by a more or less abstract argument, that the earth is spherical, he says:

The evidence of the senses further corroborates this. How else would eclipses of the moon show segments as we see them? . . . since it is the interposition of the earth that makes the eclipse, the form of this line [*i.e.*, the earth's shadow on the moon] will be caused by the form of the earth's surface, which is therefore spherical.

He, also, points to the apparent change in altitude of the stars as one travels north or south and concludes that "not only is the earth circular, but it is a circle of no great size." He then quotes the figure 400,000 *stades* (about 10,000 miles) as the circumference (diameter ?) of the earth, as determined by "mathematicians" and remarks, "This indicates . . . that, as compared with the stars, it [the earth] is not of great size."

Indeed, Aristotle, in spite of his own misty philosophising, places, in theory if not in his own practice, great emphasis on the importance of facts in connection with scientific development. For, in a paragraph in "De Generatione et Corruptione" (Book I, Chap. II), he states:

Lack of experience diminishes our power of taking a comprehensive view of the admitted facts. Hence those who dwell in intimate association with nature and its phenomena grow more and more able to formulate, as the foundation of their theories, principles such as to admit of a wide and coherent development; while those whom devotion to abstract discussions has rendered unobservant of the facts are too ready to dogmatize on the basis of a few observations.[1]

This is surely good doctrine even for twentieth-century scientists.

An attempt to summarize Aristotle's views on physics is beyond the scope of this book,[2] but reference may be made to two of his doctrines because of their bearing upon subsequent history.

The first is his views on falling bodies. In "De Caelo" (Book III, Chap. II), in the course of his proof that every body must have a finite (*i.e.*, neither infinite nor zero) weight, he says:[3]

Suppose a body A without weight, and a body B endowed with weight. Suppose the weightless body to move a distance CD, while B in the same time moves the distance CE, *which will be greater since the heavy thing*

[1] Taken from the English translation by H. H. Joachim.

[2] A summary of Aristotle's works is given by W. D. Ross in his book "Aristotle." Methuen and Company, London (1923). The reader will also find it very interesting to consult the English translation of the works of Aristotle, under the editorship of W. D. Ross. The Clarendon Press, Oxford.

[3] Quoted from the English translation by J. L. Stocks.

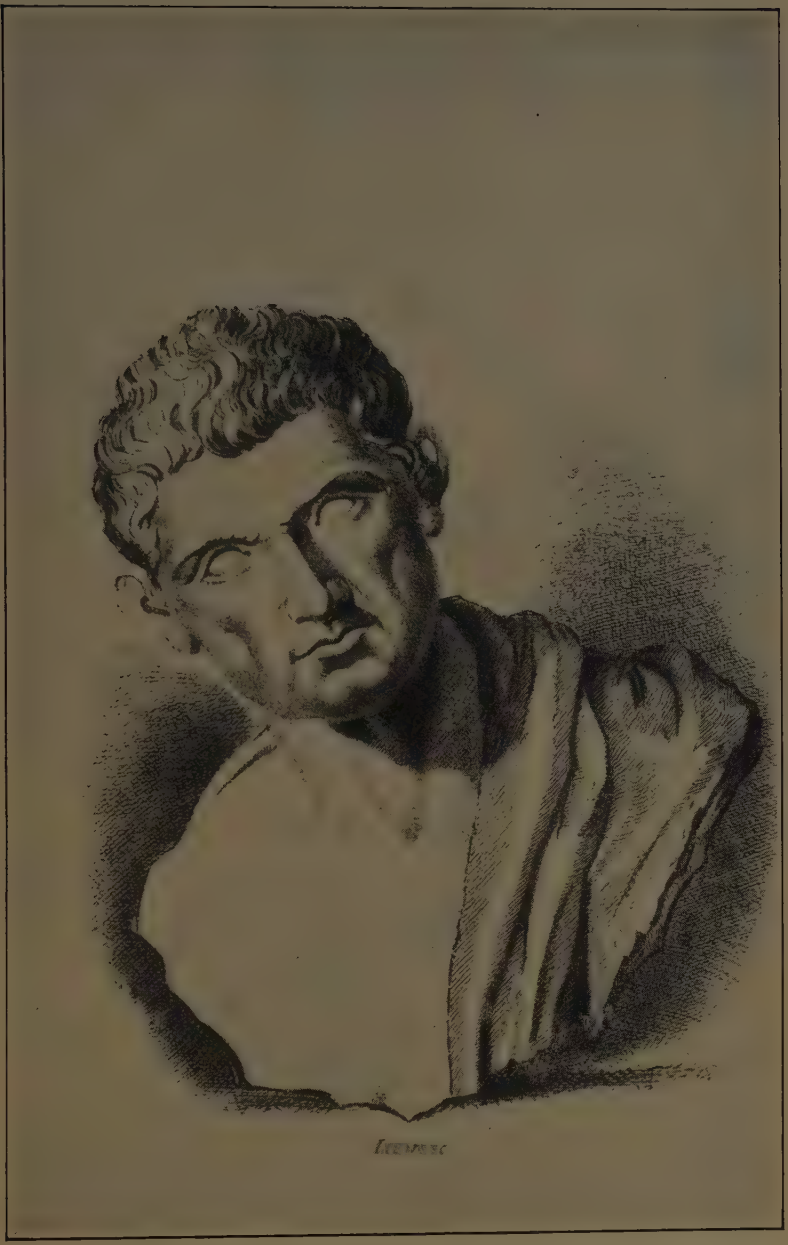

PLATE 1.—Aristotle.

(*Facing page* 10)

must move further. Let the heavy body then be divided in the proportion $CE : CD$ (for there is no reason why a part of B should not stand in this relation to the whole). Now if the whole moves the whole distance CE, *the part must in the same time move the distance* CD.

And in the "Physica" (Book IV, Chap. VI), in connection with the proof that there is no void separate from the bodies, appears an argument which, paraphrased by Ross, runs as follows:

Speed of movement varies in the ratio of the weight of the moved body to the resistance of the medium. Therefore (*a*) that which passes through a void [*i.e.*, zero resistance] should take no time to do so, and (*b*) a light body should take no longer to move through the void than the heavy one. But in fact nothing moves in no time, and *heavy bodies always move faster than light ones.*

These two references illustrate Aristotle's belief that a heavy body will move (fall?) more rapidly than a light one, a doctrine which was held unquestioned until Galileo's famous experiment at the leaning tower of Pisa.

The second doctrine referred to is that of the motion of the earth, sun, and planets. Aristotle, in his "De Caelo" (Book II, Chap. XIV), after a series of abstract arguments, in the course of which he states that "heavy bodies forcibly thrown quite straight upward return to the point from which they started, even if they be thrown to an infinite (!) distance," concludes "that the earth does not move and does not lie elsewhere than at the center." That is, the earth is immobile and in the center of the universe, which, according to him consists of a series of concentric spheres containing, and causing, the motion of the sun, planets, and stars. The authority of Aristotle was so great as completely to overshadow the theory of Philolaus that the earth moves round a central fire and to render sterile the brilliant work of Aristarchus, who, in the century following Aristotle, proposed a cosmogony essentially in agreement with the modern Copernican system. Concerning Aristotle's views on other branches of physics, little comment is necessary. His theory of vision coincided with that of Democritus and Empedocles, but he rejected the atomic theory of Democritus. In his "Mechanica"—probably not written by Aristotle himself—is found a discussion of levers, pulleys, wedges, and the like. The doctrine of inertia is raised by the question (Chap. XXXIII): "How is it that a body is carried along by a motion not its own, if that which started it does not keep following and pushing it along?" But his answer quite misses the point, for he says that

the original impelling force pushes one thing (*i.e.*, air or other medium in which the motion occurs), "and this in its turn pushes along something else," and it finally comes to rest "when the weight of the moving object has a stronger inclination downward than the force of that which pushes it." And yet, as previously quoted, Aristotle clearly recognized the effect on motion of the "resistance of the medium."

9. Euclid (last half of fourth century B.C.), in addition to his mathematical works, wrote two books on optics, the "Optics" and the "Catoptics." These are largely mathematical and assume vision to be due to particles emitted from the eye. He treats of visual angles and apparent size of objects and correctly enunciates the modern law of reflection.

10. Aristarchus (about 310–230 B.C.) was an astronomer and mathematician rather than a physicist, but his enunciation of a cosmogony identical with that proposed by Copernicus 2,000 years later commands our attention, because of its relation to Newton's discovery of the law of gravitation. What led Aristarchus to this discovery, we are not told. Indeed, no mention of this hypothesis is made in his only extant work, "On the Sizes and Distances of the Sun and Moon." But in a book called "The Sand-reckoner" by Archimedes, 25 years younger than Aristarchus, we are told that "Aristarchus of Samos brought out a book" containing the hypothesis "that the fixed stars and the sun remain unmoved; that the earth revolves around the sun in the circumference of a circle, the sun lying in the middle of the orbit"; and that "the sphere of the fixed stars" is very great compared to the circle in which the earth revolves. The theory is similar to that of Philolaus, in that both, discarding the then-prevalent idea that the earth is fixed in the center of the universe, make the earth simply one of the planets. The theory is a far-reaching improvement over that of Philalaus, in that *it dispenses with all the unknown in the universe*—the central fire—and *builds a cosmogony out of known heavenly bodies* only. But the prestige of Aristotle was too great, and the geocentric hypothesis which he supported was so completely satisfactory to the ancient mind, that Aristarchus' theory was practically lost for nearly 2,000 years.[1]

[1] HEATH, T. L.: "Aristarchus of Samos," an exceedingly interesting and valuable book (previously referred to). It contains a review of early Greek astronomy up to the time of Aristarchus, a discussion of his work, and a translation of his only extant book, "On the Sizes and Distances of the Sun and Moon."

11. Archimedes (287–212 B.C.), whose name is known to every student of elementary physics because of the famous principle of hydrostatics which bears his name, was one of the most noted physicists of antiquity. He was a man of great ability in what would now be called "theoretical (or mathematical) physics" as well as a practical engineer—a sort of ancient Lord Kelvin. Of his nine extant works, six deal almost exclusively with mathematics, mostly geometry, and three touch the subject of physics, namely, "On the Equilibrium of Planes," "The Sand-reckoner," and "On Floating Bodies." In the first of these are developed numerous propositions relative to the center of gravity. In the second, he computes that 10^{63} grains of sand would fill the sphere of the universe, as fixed by Aristarchus. In "On Floating Bodies," by a series of propositions, is laid the foundations of hydrostatics. His Proposition 7 enunciates the famous principle: "A solid heavier than a fluid will, if placed in it, descend to the bottom of the fluid, and the solid will, when weighed in the fluid, be lighter than its true weight by the weight of the fluid displaced." Indeed, so apt and accurate was Archimedes' application of mathematics, that he might be called the founder of mathematical physics.

12. From the Greeks to Copernicus.—To give but a passing comment to the 17 centuries between Archimedes and Copernicus would seem to give the reader the impression that no developments of moment occurred during that long period. This impression is almost, *but not quite*, correct. The one important exception is in the field of optics—geometrical optics, not physical optics. Ptolemy of Alexandria (70–147 A.D.) collected the optical knowledge of his time in book form. This treatise discusses, among other things, reflection from mirrors—plane, convex, concave—and, particularly, refraction, which Ptolemy seems to have studied experimentally. He states, qualitatively, the correct laws of refraction (*i.e.*, the bending of the refracted ray toward or away from the perpendicular on entering a more dense or a less dense medium). He gives, in degrees, relative values of angles of incidence and of refraction for air-water, air-glass, and water-glass surfaces, and he describes an apparatus by which he determined these quantities. He states that for a given interface these two angles are proportional. He also mentions atmospheric refraction as affecting the apparent position of stars—a discovery attributed to Cleomedes, some decades earlier.

From Ptolemy to the Arabian, Al Hazen (who died about 1038 A.D.), is a span of 9 centuries—*twice* the total lapse of time from the discovery of America to the present—during which there was stagnation in almost all lines of intellectual pursuits. But about the eighth century A.D., as an indirect result of religious activity, the Arabs began to cultivate chemistry, mathematics, and astronomy, in large part by translating into Arabic the works of the Greeks. And in a few instances, the Arabs made original contributions. It was under these influences that Al Hazen, following the exposition set forth by Ptolemy and his predecessors, produced a work on optics in seven books. This treatise sets forth a clear description of the optical system of the eye; discusses the laws of concave, and convex mirrors, both spherical and cylindrical; and carries the subject of refraction a little farther than Ptolemy carried it by recognizing that the proportionality between the angles of incidence and refraction holds only for small angles.

But from the time of the Greeks until the sixteenth century, there were practically no developments in physics worthy even of passing comment. The authority of the Greeks was supreme. Then came a period of intense intellectual activity—the Renaissance. And then were produced such men as Copernicus, Tycho, Kepler, Galileo, Newton, who, with their contemporaries and colleagues, in a space of hardly more than a century, completely broke the "spell" of Greek prestige and made possible the beginnings of modern experimental science. In so far as the heliocentric theory completely revolutionized man's conception of the universe, and his place in it, it is quite correct to regard the work of Copernicus as beginning a new era in scientific thought. But had it not been for other discoveries coming immediately after Copernicus, such as the telescope, Kepler's laws. Galileo's famous experiments on falling bodies, and many others, it is quite possible that the theory of Copernicus would have had the same fate as that of Aristarchus centuries earlier. It is, therefore, fitting to regard the birth of the Copernican theory as *closing* the first period in the history of physics.

13. The Copernican System.—Copernicus was born in Thoru, in Polish Prussia, on Feb. 19, 1473. (He is, therefore, to be thought of as a younger contemporary of Columbus.) At the age of eighteen, he entered the University of Cracow, remaining there three years, during which he studied, among other subjects,

mathematics and astronomy. In 1496, he entered the University of Bologna, where he studied astronomy under the famous di Novara, who, by his support of the Pythagorean system of the universe as against the Ptolemiac, probably gave Copernicus the germ of the idea which later made him famous. After studying at Padua and at Ferrara, from which he received the degree of Doctor of Canon Law in 1503, he returned to his boyhood home, Ermeland, where he lived most of the rest of his life, as one of the leading canons at Frauenburg, near the mouth of the Vistula. "He was a quiet, scholarly monk of studious habits and with a reputation that drew to him earnest students who received viva voce instructions from him."[1] He died May 24, 1543.

Copernicus' chief contribution to science is his famous "De Revolutionibus Orbium Coelestium," in the preparation and revision of which he spent nearly 30 years, and which was printed just at the close of his life. In this book, Copernicus boldly proclaims the heliocentric world system, as against the Ptolemaic. How he came to devise the new system we are not told; we can only surmise. But it is almost certain that the *idea* of a moving world was not original with him. He was doubtless familiar with the theories of Aristarchus,[2] and, indeed, in the preface of "De Revolutionibus," after pointing out the extremely unsatisfactory status of astronomical theories, he says:

> Wherefore I took upon myself the task of re-reading the books of all the philosophers which I could obtain, to seek out whether any one had ever conjectured that the motions of the spheres of the universe were other than they supposed who taught mathematics in the schools.

He found that Cicero referred to the theory of Nicetus that the earth moved; that "according to Plutarch, certain others had held the same opinion." These "others" were Philolaus, Heraclides, and Ecphantus. "When from this, therefore," he continues, "I had conceived its possibility, I myself also began to meditate upon the mobility of the earth." Copernicus was, also, familiar with the work of two astronomers of the previous generation, Pürbach (1423–1461) and Regiomontanus (1436–1476), who, although they themselves accepted the Ptolemaic theory, nevertheless convinced themselves that the actual posi-

[1] LODGE, OLIVER: "Pioneers of Science." Quotation from "Copernicus and the Earth's Motion."

[2] HEATH: "Aristarchus of Samos," p. 301.

tions of the planets in the sky differed very considerably from the places computed from the existing astronomical tables based on Ptolemy. Further, and from the historian's point of view *very* important, impetus was given to the study of astronomy by the ever increasing demands of navigators, who were obliged to trust entirely to the stars and the compass and who, therefore, required as perfect a theory as possible of the motions of the heavenly bodies.

Copernicus perceived that, by assuming that the earth is a planet, like the others, and that all the planets move round the sun, a great simplification, both philosophical and mathematical, could be made with regard to the world system. He could, thus, easily account for the seasons and for the apparent retrograde motion, at times, of the planets. The rotation of the earth on its axis caused the *apparent* daily motion of the sun, moon, and stars, and he pointed out that, probably, the stars were too far away for any (annual) motion of the earth to affect their apparent places. He gave the correct order of the planets from the sun outward.

In the absence of data to the contrary, he assumed that the planets moved in uniform circular motion around the sun, instead of in ellipses, as Kepler, using the accurate observations of Tycho, later showed.

Whatever the system as proposed by Copernicus lacked quantitatively, it was correct, in its main outline, qualitatively. Its reasonableness set a few men thinking and did much to usher in a new era in science, an era which could come only when truth could have the opportunity of standing alone, *unaided* or *unhindered* by the "authority" of 2,000 years.

CHAPTER II

HISTORICAL SKETCH, SECOND PERIOD (1550-1800 A.D.): THE RISE OF THE EXPERIMENTAL METHOD

1. The Growing Dissatisfaction with Authority.—Copernicus, by announcing his heliocentric world system, may be said to have spoken the prologue preceding the rise of the curtain on modern physics revealing among the first actors, Galileo, Tycho and Kepler. But certain details of the stage setting must not be forgotten. A few men were beginning to show dissatisfaction with existing conditions in science, dominated as it then was by ancient Greek dogma and "authority."

Two centuries before Copernicus, Roger Bacon (1214–1294), British philosopher and scientist and a monk of the Franciscan Order, taught that in order to learn the secrets of nature *we must first observe.* He believed in mathematics and in deductive science, but he clearly realized that only as these were based on observed phenomena and tested by experiment could useful knowledge result. "In an age where experimenting was sure to cost a man his reputation and was likely to cost him his life, he insisted on experimenting and braved all risks;"[1] with the result that he spent 24 of the last 37 years of his life in prison—one of the many "martyrs of science."

Then there was Leonardo da Vinci (1452–1519), Italian painter, architect, sculptor, engineer, and philosopher, whose greatness as a scientist has come to be appreciated only in recent years, for his works were left in manuscript form and were probably not widely known among his contemporaries—for which reason his influence on early science is comparatively insignificant. Nevertheless, da Vinci is generally regarded as one of the world's greatest thinkers. His belief in the value of experiment is worthy of the twentieth century: "Experience," he writes "never deceives; it is only our judgment which deceives us." Or, again: "Before making this case a general rule, test it by experiment two or three

[1] White, Andrew D.: "History of the Warfare of Science with Theology."

times, and see if the experiment produces the same effect."[1] Although expressed in the vague language of his time, some of da Vinci's ideas concerning what we now refer to as "force," "inertia," "acceleration," the "laws of motion," etc., were qualitatively correct. For example, as regards velocity and acceleration, he says:

> In the air of uniform density, the heavy body which falls acquires at each stage of time a degree of movement more than the degree of the preceding time and likewise a degree of velocity more than the degree [of velocity] of the preceding time. Then to each quantity doubled in time the length of the descent is doubled, likewise the velocity of the movement.

That is, in the case of a falling body, he held correctly that the velocity is proportional to time of fall, but he did not grasp the significance of this in connection with the total distance covered. He wrote about levers, inclined planes, pulleys, flight of birds, and mechanical flight. Concerning perpetual motion, he wrote: "Oh, speculators on perpetual motion, how many vain projects of the like character you have created! Go and be the companions of the searchers after gold." Rejecting the Ptolemaic theory, he held that "the sun does not move." That he was not persecuted, or even burned at the stake, as was Bruno, a century later, for holding such revolutionary and, therefore(!), heretical, views is probably due to the fact that his doctrines were given so little publicity; for, holding no academic position, he did not teach, and he published nothing. Could his successors have known of his work, how great an impetus might have been given to the growth of science! We shall see a similar situation in the work of Henry Cavendish in the latter part of the eighteenth century.

The unrest typified by the doctrines of Copernicus, Roger Bacon, Da Vinci, and others culminated in the work of Galileo and of Tycho and Kepler. Galileo is usually thought of as a physicist, and Tycho and Kepler as astronomers. Although Tycho was the oldest of the three, we shall discuss Galileo first.

2. Galileo Galilei (1564–1642).—Galileo is widely, and quite correctly, regarded as the father of modern physics. To be sure, physics had grandfathers and still more remote ancestors, but

[1] HART, IVOR B.: "The Mechanical Investigations of Leonardo da Vinci." The Open Court Publishing Company, Chicago.

none of them gave to physics, particularly to experimental physics, so much as Galileo.

He was born in Pisa, Feb. 15, 1564—about the time of the founding of the first permanent American settlement, St. Augustine, Florida, in 1565. He was descended from a noble family, and it is quite probable that he inherited from his father the spirit of free inquiry which characterized his life. For in the writings of the elder Galileo, who was well educated and was an accomplished musician, appears the statement: "It appears to me that they who in proof of any assertion rely simply on the weight of authority, without adducing any argument in support of it, act very absurdly."

At the age of twelve, Galileo was sent to the monastery of Vallombrosa, near Florence, where he studied Greek, Latin, Logic, and other "Humanities." He was apparently a brilliant and a versatile student, for he excelled in classics and literature and was something of a poet, musician, and art critic. He also showed an aptitude for science and exhibited considerable mechanical inventiveness.

It was decided that a medical career was more in keeping with his intellectual attainments than were mercantile pursuits, and young Galileo, at the age of seventeen, was sent to the University of Pisa to study medicine. It was here that he made his first discovery and invention. One day, in 1581, he noticed the regular oscillations of the great bronze (hanging) lamp, in the cathedral at Pisa. Although the amplitude of these oscillations became less and less, they were all performed in the same time, as he determined by counting his pulse. Turning the process around, he invented a "pulsometer," a ball-and-string (*i.e.*, simple pendulum) device, whose length, when adjusted to synchronism with the pulse, was a measure of its frequency.

But the urge toward mathematics and science overcame the pecuniary advantages of a medical career, and, eventually, Galileo, at the age of twenty-six, became professor of mathematics at Pisa, where he began a systematic investigation of the mechanical doctrines of Aristotle. He soon demonstrated experimentally to his own satisfaction that Aristotle was in error in many of his assertions, and these errors he proclaimed energetically from his professorial chair. Now, to doubt Aristotle, or any other ancient authority, was heresy, and Galileo soon brought upon himself the enmity of many of those who should

have been his colleagues and supporters. To convince these that, in at least one particular, it was easy to demonstrate that Aristotle was in error, Galileo performed the most famous experiment in all history, the dropping of two bodies of different weight from the leaning tower of Pisa.

It had been pointed out above (Chap. I, Sec. 8) that Aristotle had taught that a heavy body would fall more rapidly than a light one. Galileo had, by experiment, proved this doctrine to be wrong. He thought that he could convince his opponents and, perhaps, shake their implicit faith in Aristotle, by an appeal to their senses. So, one morning, he ascended the leaning tower of Pisa, taking with him a 1-pound shot and a 10-pound shot (some writers say 100 pounds). These he dropped simultaneously before the expectant multitude. They fell together and struck the ground with a single thud. A few were convinced that Galileo was right and that Aristotle was wrong. But the vast majority rubbed their eyes, looked up their Aristotle, and found, chapter and verse, that *he* said that the heavier body would fall more quickly. Therefore Galileo *must* be wrong.

And then began a persecution which was to last Galileo's lifetime, increasing in severity as he grew older, and, finally, resulting in imprisonment. To present the details of his stormy life is far beyond the scope of this book. The reader is referred to his biographers.[1]

He was soon forced to quit Pisa and, in 1592, became Professor of Mathematics at the Venetian University of Padua, where he remained 18 years, enjoying comparative liberty of thought and teaching. His fame as a teacher spread all over Europe, and his lectures were crowded. To this period belongs his invention (1602) of the air thermometer; also, a military and geometrical compass.

In October, 1608, a Dutch optician, Lipperhy, as a result of a chance observation of an apprentice, had succeeded in "making distant objects appear nearer but inverted" by looking through a tube in which were mounted two spectacle lenses. News of this invention—but *not* a sample of the instrument—reached Galileo in June, 1609. Immediately grasping the principle involved, he made a telescope and exhibited it in Venice "for

[1] FAHIE, J. J.: "Galileo: His Life and Work" (1903).
BREWSTER, SIR DAVID: "Martyrs of Science" (1870).
LODGE, OLIVER: "Pioneers of Science."

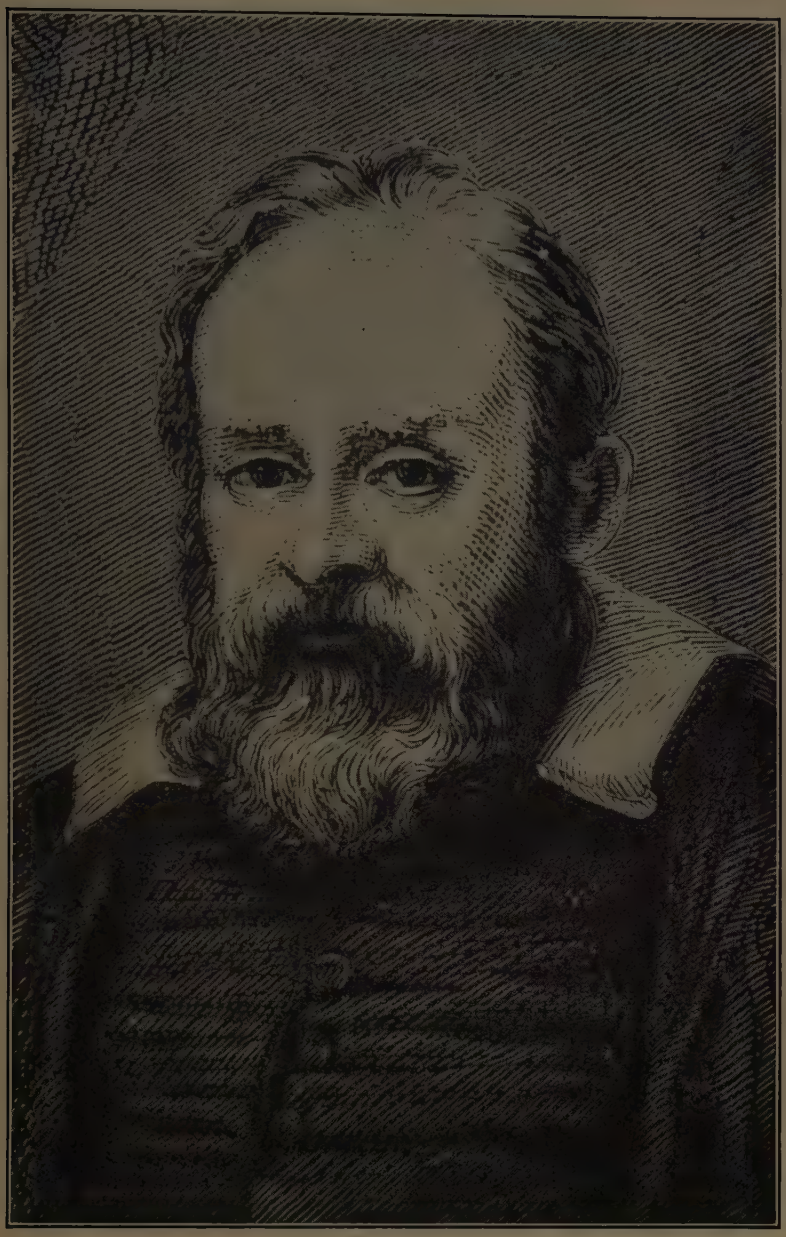

PLATE 2.—Galileo.

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more than a month to the astonishment of the chiefs of the republic." Within a short time, he made a better instrument, with a magnifying power of 20 diameters, and by January, 1610, a still more powerful one with a power of 30 diameters.[1]

With this instrument, he made a number of the most fundamental discoveries. He observed the mountains on the moon and made a reasonably close estimate of their altitude. He saw that the number of fixed stars was vastly greater than could be seen by the unaided eye and, thus, was able to explain the age-long puzzle—the Milky Way. He saw that the planets appeared, in his telescope, as luminous disks, while the stars still remained points of light.

But the most important of these astronomical discoveries was that of the moons of Jupiter. On Jan. 7, 1610, he directed his telescope toward Jupiter and noticed three stars near the planet, one on the west and two on the east. On the following night, they were all on the west side and nearer to each other. On Jan. 10, only two of the stars were visible, and they were both on the east side! Galileo concluded that these "stars" were really satelites of Jupiter, and, by Mar. 2, he had determined their periods. These discoveries naturally made Galileo famous, and he soon accepted an invitation to return to Pisa as "First Mathematician and Philosopher," at a very substantial increase in salary, although at a sacrifice—and a very unfortunate one, as it turned out—of his "academic freedom" in Padua. Continuing his astronomical investigations, he discovered the crescent phases of Venus, sunspots and the rotation of the sun, the faculæ of the solar atmosphere, and the libration of the moon. In 1612, he published his "Discourse on Floating Bodies."

At first, it seemed as if his fame had silenced all opposition from the Church. But the support which his discoveries gave to the hated Copernican theory and his vigorous attacks on Aristotelian philosophy roused his enemies to fury; with the result, that, in 1615, he was hauled before the Pope and, under threat of imprisonment and torture, was "enjoined . . . to relinquish altogether the said opinion that the sun is the center of the world and immovable . . . nor henceforth to hold, teach or defend it in any way . . . " Simultaneously, it was decreed that the

[1] Galileo's telescopes were similar to the modern opera glass—a double-convex (or plano-convex) object glass and a double-concave eyepiece. Hence they had an erect image, unlike the Dutch instrument.

works of Copernicus "be suspended until they be corrected." Galileo acquiesced in these decrees and was allowed to return to Pisa, where he continued his researches along such lines as would not give offense.

In 1623, one of Galileo's friends, Barberini, became Pope Urban VIII, from whom Galileo received assurances of "pontifical good will." Thereupon, thinking that the decree of 1615 would no longer be enforced, he began the writing of his great book, "Dialogues on the Ptolmaic and Copernican Systems," which was published in 1632, *under formal permission from the censor*, the "Master of the Sacred Palace," who "signed the license with his own hand."[1]

The form of these dialogues is ingeniously contrived to abide by the *letter* of the decree of 1615. Three "characters" carry on the discussion: Salviati, a Copernican; Simplicio, an Aristotelian; and Sagredo, a witty, impartial, good-natured chairman. The dialogues cover 4 "Days," during which the arguments for and against each system are set forth with apparent impartiality and without reaching any *stated* conclusion. Nevertheless, the general effect of the book was "a powerful plea for Copernicanism."[2]

But, in spite of its enthusiastic reception by the public, its form did not deceive his enemies, who were now determined that he must be silenced. But how could this be accomplished as long as the Pope was Galileo's friend? Very easy: Make the Pope an enemy of Galileo! This was very effectually accomplished by representing (of course, falsely) to the Pope that the Simplicio of the dialogues, whose ignorance was very apparent, was simply a caricature of the Pope himself. In spite of the absurdity of the argument—for Galileo would hardly have risked offending Urban VIII, his one friend in the Church—the Pope's weakness, vanity, arrogance, and ambition so beclouded his senses that he was easily convinced that Galileo "had made game of him." Whereupon he was ready to join Galileo's enemies in persecuting that great scientist, *ostensibly* for "the safety of the Church and the vindication of its decrees."

This tragic incident—the alienation of the Pope's friendship—is illustrative of the fact that, in the seventeenth just as in the

[1] FAHIE: "Galileo and His Works." Letter from Galileo to Cioli, Mar. 7, 1631.

[2] FAHIE, *loc. cit.*

twentieth century, much of the "warfare between science and theology"—as Andrew D. White calls it[1]—has been based upon personal ambition and revenge rather than upon a sincere wish to uphold theological doctrines. In 1612, the Pope—he was then Cardinal Barberini—upon a receipt of a copy of the work, "On Floating Bodies," had written Galileo:

> I have received your treaties . . . and shall read them with great pleasure, both to confirm myself in my opinions, which agree with yours, and to enojoy with the rest of the world the fruits of your rare intellect.

In 1613, Barberini had complimented Galileo very highly for his work on sunspots and, in 1620, had composed some verses, celebrating Galileo's discoveries, which he sent to Galileo, writing, "I propose to add lustre to my poetry by coupling it with your renowned name." Late in 1623, Galileo published "Il Saggiatore," which he dedicated to Barberini, then Pope Urban VIII, who was so delighted with it that he "had it read aloud to him at table."[2] The Pope as Galileo's friend could apparently not only applaud but also heartily concur in Galileo's doctrines and teachings. But the Pope as Galileo's enemy could join, with all his might, in declaring those same doctrines to be so dangerous and inimical to the (*supposed!*) teachings of Holy Scripture as to warrant bringing Galileo before the Inquisition, which, some 30 years before, had burned Bruno at the stake.

These personal motives, which have been the cause of so much opposition to new scientific advances, are to be found not only in all branches of the Church, Protestant as well as Catholic, but also even among scientists themselves, as we shall see later. Intolerance, even when it is sincere, is to be condemned; but *insincere* intolerance is to be despised. Yet, one cannot fully comprehend the forward march of science unless one recognizes the seriousness of obstacles of this kind which have had to be overcome. Great as is the fame of Galileo, how much more might he have accomplished if the energy which he was forced to spend in overcoming opposition might have been directed toward his researches. Without doubt, the giant strides which are being taken by science in this twentieth century are made possible, in part at least, by the freedom which the scientist now enjoys. How absurd it would be for *anyone* to criticise the

[1] WHITE, ANDREW D.: "The History of the Warfare between Science and Theology."

[2] FAHIE, *loc. cit.*

Bohr theory of atomic structure because it is mentioned neither by Aristotle nor the Bible!

With this array against him, it was inevitable that Galileo should be called before the Inquisition. He was now sixty-seven years old, impaired in health and in spirit, if not in intellect. Bowing to the inevitable because of the magnitude of the forces arrayed against him, which forces included his former friend the Pope, and perhaps with the memory of Bruno all too clear, he followed the advice of his friends and indicated his "free and unbiased" willingness to recant, to "abjure, curse and detest the said heresies and errors and every other error and sect contrary to the Holy Church" and he further agreed "never more in future to say, or assert anything, verbally or in writing, which may give rise to a similar suspicion."

Perhaps out of respect for his age and infirmities, perhaps because the Pope remembered, with a bit of shame, his former friendship, Galileo was not imprisoned and tortured but was "detained" in Rome, under suspended sentence. Ultimately, he was allowed to return to his home at Arcetri, although still as a prisoner. Here, during the last years of his life, he prepared and, in 1636, published his "Dialogues on the Two New Sciences"[1] (*i.e.*, Cohesion and Motion).

These dialogues on "Motion" sum up Galileo's earlier experiments and his more mature deliberations. He states that "if the resistance of the media be taken away, all matter would descend with equal velocity." He correctly describes, and deduces the formulæ of, uniformly accelerated motion. He shows that the path of a projectile is parabolic under the limiting conditions (1) that the path is small compared to the dimensions of the earth and (2) that the motion either takes place *in vacuo* or is comparatively slow. He states that, if all resistance were

[1] See the excellent translation by Crew and de Salvio.

Some writers have severely censured Galileo for yielding to the Inquisition. They say that "had Galileo added the courage of a martyr to the wisdom of a sage . . . science would have achieved a memorable triumph" (see BREWSTER: "Life of Newton." Whatever opinions on this question one may hold, one fact stands out indisputable: Had Galileo *not* yielded he would surely have been cast into the dungeon, and would probably have been burned at the stake. His working days would have been over. We should not have had handed down to us these dialogues on Motion, so fundamental to our modern physics.

removed, a body projected along a horizontal plane would continue to move forever. And, indeed, he paved the way for the enunciation, by Newton, of the famous three laws of motion, the foundation of mechanics. He describes an attempt to measure the velocity of light by two observers, a mile apart, one of whom uncovers a lantern as soon as he perceives the other to cover up his lantern. No greater elapsed interval was observed at a distance of a mile than at short distances. Not convinced, however, that light travels instantaneously, Galileo recommended that the experiment be tried, with the aid of a telescope, at greater distances. It is, perhaps, worthy of remark that the "toothed-wheel" experiment of Fizeau, performed in 1849, is, in a sense, similar to this method proposed by Galileo.

Galileo's sight began to fail, and, by 1638, he was totally blind. Nevertheless, his mind continued active, and, in 1641, with the aid of two assistants, Torricelli and Viviani, he prepared some additional material for his dialogues.

He died Jan. 8, 1642, only a few months before the birth of that other great physicist of this second period, Isaac Newton.

How much the modern world owes to Galileo, perhaps few of the present day realize. Physicists, at least, should be acquainted with the main details not only of his scientific work but also of his life. The student is, therefore, urged to peruse one of the several biographies and, also, to read some of Galileo's writings, if not in the original Latin, then in translation. Even a short time spent in following his deductions and in reading *first hand* something which he wrote will prove both interesting and valuable.

3. Tycho (1546–1601) **and Kepler** (1571–1630).—While Galileo was carrying on his investigations in Italy, two other European scientists, Tycho and Kepler, were making astronomical studies of the most fundamental character. The work of these two men is particularly interesting, not only because of its direct bearing on the development of physics but also, more particularly, because of the mutual dependence of the work of each upon that of the other, a relation very common in present-day science. Tycho was the experimentalist, the observer, who supplied the accurate data upon which Kepler, the theoretically inclined, built his theory of planetary motion. Tycho's observations were, of course, of empirical value, but, without a Kepler to build a theory from them, they would have attracted hardly

more than passing notice. Kepler, in turn, might have theorized to his heart's content, but without the accurate data of a Tycho, those theories would ultimately have shared the fate of Aristotle's. Sometimes, theory precedes; sometimes, experiment. But neither can get far without the other.

Tycho Brahe was born of a noble family in Scania (the southern part of Sweden, belonging at that time to Denmark), on Dec. 14, 1546. When just past twelve years of age, he was sent to the University at Copenhagen, where he studied rhetoric and philosophy, in contemplation of a career as statesman, for which his uncle, who assumed responsiblity for Tycho's upbringing, desired him to prepare. But his attention was directed toward astronomy by a partial eclipse of the sun, in 1560, and, during the remainder of his three years at Copenhagen, he studied Ptolemy, Euclid, and allied authors.

In 1562, the uncle, thinking to remove him from the influences which were rapidly taking him away from the life of a statesman, sent him to Leipzig, where, in spite of instructions to the contrary, Tycho, at times in secret, continued his astronomical studies. He soon discovered the incorrectness of the current astronomical tables. In August, 1563, occurred a conjunction of Saturn and Jupiter, of which Tycho made careful observations. During this time, he dabbled in astrology, because of the then very prevalent belief that human affairs are materially influenced by the position of the planets; just as vegetable life depends on the position of the sun in the ecliptic (*i.e.*, winter or summer).

After several years of study and travel, during which time he acquired a notable reputation as an astronomer, Tycho was settled by King Frederick II of Denmark upon the Island of Hveen, in 1575. Here the king built the celebrated observatory of Uraniborg and guaranteed Tycho an income to enable him to carry on his observations. In return for this assistance, Tycho made astrological calculations for the royal family and acted as scientific advisor. The observatory was equipped with the most elaborate and beautiful instruments, and for over twenty years Tycho remained at Uraniborg, making systematic observations of the planets, constructing a star catalogue, and accumulating other astronomical data, always with the highest possible order of accuracy and with the hope ultimately of reforming astronomy.

In 1597, Tycho was compelled to leave Uraniborg, having incurred the displeasure of the government, because, it was alleged, he was careless in carrying out the various duties incumbent on him in return for his grants of income. In 1599, he entered the service of the German emperor, Rudolph the Second and, in due course, made plans to establish an observatory at Prague, with his instruments from Uraniborg and a corps of assistants. These plans were hardly more than well underway when Tycho suddenly died, Oct. 24, 1601.

Among the assistants attracted to Tycho's observatory at Prague was a brilliant young mathematician, Johann Kepler, with whom Tycho had corresponded for several years. Kepler was born at Weil, in Wurtenburg, Dec. 21, 1571. At the age of twenty, he took the Master's degree at the University of Tubingen, where, under the mathematician Mästlin, he became acquainted with the theories of Copernicus.

In 1594, Kepler accepted a lectureship at Gratz. This post he held for five years, devoting most of his time to astronomy. Among the questions which he attacked, initially without success, was that of a possible relation between the periods of revolution of the then-known planets and their distances from the sun. Being compelled to leave Gratz because of certain religious decrees, Kepler finally became an assistant to Tycho at Prague, late in 1600. This association lasted only a few months, being cut short by Tycho's sudden death. Whereupon Kepler succeeded Tycho as principal mathematician to the emperor and undertook the completion of several projects which Tycho had underway. Chief among these were the new astronomical tables based on Tycho's elaborate observations. After many delays, these were finally published as the Rudolphine Tables, in 1628, in honor of Emperor Rudolph, who had established Tycho at Prague.

Kepler remained at Prague until 1612, when he accepted a professorship at Linz. This post he held almost until his death in November, 1630.

The contrast between Kepler's life and that of Tycho is striking, indeed. Tycho was of noble birth, was rich, vigorous, of great mechanical ingenuity and experimental skill. Kepler was sickly, lacked experimental ability, and was, throughout his life, harassed by poverty and misfortune. Yet he possessed a speculative imagination and mathematical perception of very

high order. He believed thoroughly in the Copernican system, which Tycho rejected for a system of his own in which the sun with his family of planets revolved once per day around the stationery earth, the planets (except the earth) revolving around the sun. It is one of the dramatic situations in science that Tycho's data on planetary motions, taken in support of his own theory, became, in the hands of Kepler, the clinching argument for the Copernican system.

At Prague, Kepler made a special study of the motion of Mars, using Tycho's observations taken so carefully at Uraniborg. At first, he tried to reconcile the various recorded positions of the planet by assuming that the circumsolar orbits of both Earth and Mars were circles. He tried various orbits in various relative positions with respect to the sun. None worked. By resorting to the Ptolemaic notion of epicycles and deferents, some improvement resulted, but still the observed positions differed from the computed, in some cases by as much as 8 minutes of arc.[1] Kepler knew that Tycho's observations could not be in error by that much. Some new concept regarding planetary motion was necessary.

All of these attempts required enormous labor, but still, in spite of the seeming hopelessness of the problem, Kepler persevered in his quest for the right orbit. Some progress was made when he gave up *uniform* circular motion and assumed that the speed varied inversely as the planet's distance from the sun. This assumption is his famous "second law:" that *the radius-vector from the sun to the planet describes equal areas in equal times.* It worked approximately, but still there were systematic errors which exceeded the possible errors of observation.

Finally, he cast aside the last traditions of the Ptolmaic system, namely, that the planets move in circles, and tried, first, an oval path and, then, an ellipse, with the sun at one focus. At last, his years of computations bore fruit. The path *was* an ellipse. Theory and observation agreed! And one of the most important and far-reaching laws in all science had been discovered, all because of a discrepancy of 8 minutes of arc between observation and theory! In fact, one of the striking things in the growth of science, particularly physical science, is the fact that a very great many fundamental advances have come about because of just

[1] About one-fourth the angular diameter of the moon viewed from the earth.

such discrepancies, frequently very small ones, between observation and theory. We shall have occasion to note this, time and again.

Another problem with which Kepler had been wrestling for many years was that of the possible relation between the periods of revolution of the several planets around the sun and the radii of their respective orbits. Long before he joined Tycho, he had speculated on this problem, possibly because he felt, instinctively, that the motions of the planets must be the result of some universal "cause." Of course, he rejected, as nonsense, the prevailing opinion that there were six planets because the number "six" was sacred! And he reasoned that it was not an accidental coincidence that whenever a gap appeared in the series of periods (as between Mars and Jupiter), there was a corresponding gap in the series of radii of the several orbits.

His first "solution" of a part of the problem is almost as fantastic as the sacredness of the number six. While lecturing at Gratz, he noted that the orbits of Jupiter and Saturn bore to each other *about* the same relation as a circle inscribed in an equilateral triangle bears to the circumscribed circle.[1] Starting from this "observation" and noting that, since there are *six* planets, there are *five* spaces between their orbits, he concluded that there must be some connection between these five spaces and the *five* regular geometrical solids. After some speculation, he hit upon the following scheme:

Start with a sphere whose great circle represents the earth's orbit. Describe around this a dodecahedron, and circumscribe around this a sphere. A great circle of this sphere represents the orbit of Mars. By similar use of a tetrahedron around the orbit of Mars, we get to Jupiter; and from Jupiter to Saturn, by a cube. An icosahedron inside the earth's orbit gets to the orbit of Venus; and an octahedron inside that gets to the orbit of Mercury. The scheme was not exact so far as giving relative values for the radii of the orbits, but Kepler thought that this might be due to erroneous values of the several planetary distances.

Kepler was delighted with this scheme and published it, in 1596, in a book, "Mysterium Cosmographicum." It was this book which brought Kepler to the attention of Tycho, who, while

[1] The latter ratio (ratio of diameters) is 2:1, while modern astronomical data gives the former about 1.85:1.

expressing appreciation of Kepler's industry, nevertheless advised him "not to build up abstract speculations concerning the system of the world but rather *first lay a solid foundation in observations and then, by ascending from them, strive to come to the cause of things.*"[1]

Kepler may have followed this advice, for it was many years later (1618) when, again with Tycho's observations at hand, he hit upon the true relation between the periods of the planets and the radii of their orbits, a relation now known as Kepler's "third law," that *the squares of the times of revolution around the sun are as the cubes of the mean orbital radii.*

Here, then, are the three laws of planetary motion which Kepler handed down to posterity and which, sweeping away epicycles, deferents, and other remnants of the Ptolmaic system, paved the way for modern astronomy:

1. The planets move round the sun in orbits which are ellipses, with the sun at one focus.

2. The radius vector (from sun to planet) sweeps over equal areas in equal times.

3. The squares of the periods of revolution of the planets round the sun are proportional to the cubes of the (mean) radii of their respective orbits, or, in algebraic symbols,

$$\frac{T^2}{R^3} = \text{constant}$$

where T is the period of the planet and R is the mean distance from the sun.

But what makes the planets move? *Why* do the outer ones go more slowly? Is there "one moving intelligence in the sun, the common center, forcing them all around, but those most violently which are nearest?" Kepler speculated long on this question, but he had only a faint glimpse of the truth, a *qualitative* idea, which Newton, with Kepler's laws and Galileo's researches on motion before him, later was able to put in *quantitative* form in the famous theory of universal gravitation. The nature of Kepler's speculations are indicated by the following extracts from the Introduction to his "Commentaries on the Motion of Mars," published in 1609:

Every corporeal substance, so far as it is corporeal, has a natural fitness for resting in every place where it may be situated by itself beyond

[1] Quoted by HART in "Makers of Science," p. 82. The italics are the author's.

the sphere of influence of a body cognate with it. Gravity is a mutual affection between cognate bodies towards union or conjunction, so that the earth attracts a stone much rather than the stone seeks the earth. . . . If two stones were placed in any part of the world[1] near each other, and beyond the sphere of influence of a third cognate body, these stones . . . would come together in the intermediate point, each approaching the other by a space proportional to the comparative mass of the other. If the moon and earth were not retained in their orbits by their animal forces or some other equivalent the earth would mount to the moon by a fifty-fourth part of their distance and the moon fall toward the earth through the other fifty-three parts . . . assuming that the substance of both is of the same density. [Then follows a hint as to the cause of the tides.] If the attractive virtue of the moon extends as far as the earth, it follows with greater reason that the attractive virtue of the earth extends as far as the moon and much farther; and, in short, nothing which consists of earthly substance anyhow constituted although thrown up to any height, can ever escape the powerful operation of this attractive virtue . . .

Unquestionably, Kepler's rough, *qualitative* concept of universal gravitation bears to the completed theory so beautifully developed by Newton much the same relation as the crude ideas of planetary motion proposed by Copernicus on the basis of the suggestion of Aristarchus bears to the *quantitative* statements contained in Kepler's three laws. Thus it is, that, in the growth of an idea or law, the qualitative phase precedes the quantitative. Sometimes, both phases come from a single mind; but very frequently, as, for example, in the case of planetary orbits and of gravitation, the completed law is the result of the efforts of several individuals, perhaps men in different generations, working "in series." The "quantum jump" seems to apply to ideas as well as to electrons!

In passing, it may be mentioned that Kepler made substantial contributions to the field of optics. He applied the law of refraction of light at small angles, previously discovered by Al Hazen,[2] to the path of a ray through a lens. And he proposed the Keplerian or astronomical type of telescope, in which a *real* image is formed, thus making possible accurate measurements by means of "cross-hairs" in the focal plane of the objective. He studied atmospheric refraction as affecting the apparent

[1] That is, the universe.

[2] That is, that for small angles the *angle* of incidence is proportional to the *angle* of refraction (see p. 14).

position of the heavenly bodies and worked out an approximate formula to allow for this error for all positions, from zenith to horizon. He understood clearly the principle of total reflection and how to determine what we now call the "critical angle." He computed the properties of hyperboloid refracting surfaces. And he was the first to propose the meniscus type of lens. In fact, his two works on optics, the "Supplements to Vitello's Optics" (1604) and the "Dioptrics" (1611), constitute by far the most systematic and original treatises on the subject up to that time.

But, again, the inevitable question: "What greater things could Kepler have accomplished if his whole life had not been harassed by ill health, poverty, and misfortune?" At least, one misfortune *was* fortunate. Kepler's expulsion from Gratz led to his association with Tycho, without which he would never have had access to that mine of data which, in the end, brought undying fame.

4. The Experimental Method Spreads.—The impetus given to science by that great trio, Tycho, Kepler, and Galileo, resulted in an ever increasing number of investigators in the generations which followed. Of great significance, too, is the fact that, at about this time, there were formed, in several European centers, various learned societies which brought together, for argument and discussion, men of kindred interests. The Lincean Society was founded in Italy, in 1603; the Royal Academy of Sciences, in France, in 1666; and the Royal Society for the Advancement of Learning, in England, in 1662. The continued improvement of the art of printing further facilitated the diffusion of scientific knowledge. Developments, in physics and mathematics, of the most fundamental importance were at hand. Mention may be made of a few of them.

Gilbert (1544–1603), an English physician, had, in 1600, published his famous work, "De Magnete," based largely upon his own experiments, in which he showed the fallacy of such popular fancies as the belief that lodestones lost their magnetic power when rubbed with garlic and regained it again when smeared with goat's blood. He was the first to recognize that the earth is a great spherical magnet, and he actually magnetized a small sphere of iron and showed that it behaved as the earth behaves. He studied frictional electricity and showed that other substances than amber are active.

Among other workers in magnetism may be mentioned Kircher (1601–1680), who, by measuring the force required to pull a piece of iron from either pole of a magnet, demonstrated the equality of the two poles; Cabeo (1585–1650), who showed that an *unmagnetized* iron needle, floated freely on water, would place itself along the earth's magnetic meridian; and Gellibrand (1597–1637), who discovered the secular variation of the magnetic declination.

In the field of optics, there was Scheiner (1575–1650), who studied the optics of the eye; Snell (1591–1626), who discovered the true law of refraction; Descartes (1596–1650), who investigated, mathematically, the form of the interface between two media, so that a point source in one should be accurately refracted to a point image in the other; Cavalieri (1598–1647), who gave the correct formula for the focal length of a thin glass lens in terms of the radii of curvature of the two sides; and Johannes Marci (1595–1667), who, by his investigations of the phenomena of refraction of light by a prism, in part anticipated Newton's discovery of the true nature of the spectrum.

Studies in acoustics were not wanting. For example, Mersenne (1588–1648), after having investigated the laws of vibrating strings, determined, in absolute measure, the frequency of a tone. He also measured the velocity of sound by observing the time interval between the flash of a gun and the arrival of the report. Similar measurements were made by Gassendi (1592–1655), who showed, also, that the velocity of the sound was independent of pitch.

There was considerable activity in the study of fluids. One of the best-known workers in this field was Torricelli (1608–1647), who studied the flow of liquids from orifices, discovered the principle of the barometer, and observed variation in barometric height with altitude. Every student of elementary physics is nowadays acquainted with the "Torricellian vacuum." Working quite independently of Torricelli, Guericke (1602–1686) invented the air pump. Pascal (1623–1662), continuing the work of Torricelli on the barometer, measured the difference in barometric height between the base and the top of a mountain, correctly explaining the reason for the difference, and, later, announced the famous principle of hydrostatics which bears his name.

Not only was physics, as a subject, beginning to assume definite form, but even the now classical subdivisions comprising mechanics, light, sound, etc., were beginning to crystalize out. Then came a man

> . . . towering head and shoulders above all his contemporaries, a veritable giant among the giants, a man whose intellect and whose contributions to knowledge are incomparably greater than those of any other scientist of the past, that prince of philosophers, Sir Isaac Newton.[1]

The other "giants" referred to, contemporaries of Newton, are such men as Boyle, Huyghens, and Hooke—names well known to every physicist.

5. Sir Isaac Newton (1642–1727).—Newton was born in the little hamlet of Woolsthorpe, England, on Christmas Day, 1642, less than a year after the death of Galileo. At the age of twelve, he was sent to the public school at Grantham, but at first he showed no exceptional aptitude for his studies. An interesting event, however, may have been the cause of his "turning over a new leaf." It is related that a schoolmate, larger than young Newton and his superior in scholarship, gave him a kick as they were going to school one morning. Newton, resenting the insult, challenged his tormentor to a fight and, though physically inferior, soundly thrashed his opponent. This victory set him thinking. He had proved his physical superiority, but he was still below his antagonist in scholarship. Thereupon, an "educational" contest ensued, in which Newton was not only successful but also actually rose to the highest place in the class.

At the age of fifteen, Newton was removed from school to assist his widowed mother in running the family estate at Woolsthorpe. But he had little taste for farming. Rather, he was interested in studying, particularly mathematics, and in devising various mechanisms. He made a water clock, waterwheels, sundials, and a working model of a windmill. And his uncle, one morning, found him under a hedge studying mathematics, when he should have been farming. Thereupon, Newton's mother wisely decided that an educational career was more suitable for her son, and he was sent back to school and, ultimately, to Cambridge, which he entered in 1661.

Of his studies at Cambridge comparatively little is known, save that he developed a fondness for mathematics and that

[1] HART: "Makers of Science."

PLATE 3.—Newton.

(*Facing page* 34)

his reading included, among other works, Kepler's "Optics," Euclid, and Descartes' "Geometry." But his creative genius soon began to appear, and before he took the degree of Bachelor of Arts (January, 1665), he had discovered the binomial theorem, developed the methods of infinite series, and discovered "fluxions," or the differential calculus.

Soon thereafter, an outbreak of the plague closed the University for some months, during which time Newton, at the family estate at Woolsthorpe, began his speculations on the subject of gravity, which, later, led to his enunciation of the inverse-square law. It was here that the much-quoted "falling apple" episode is said to have occurred, which is supposed to have given Newton the basic idea of *universal* gravitation. Of course, a falling apple *may* have started Newton's train of reasoning. Brewster, in his "Life of Newton," seems inclined to credit the story and states that he (Brewster) "saw the apple tree in 1814 and brought away a portion of one of its roots"(!) But Newton himself makes no mention of the incident, and it seems far more probable that, at Cambridge, he had read Kepler's qualitative discussion of the general principle of gravitation (quoted on p. 31) in the treatise on Mars. Certainly, *Newton was familiar with the three laws of planetary motion which Kepler announced in this book.*

In 1667, Newton returned to Cambridge as Fellow of Trinity. Two years later, at the age of twenty-six, he was appointed Lucasian Professor of Mathematics, a chair which he held for nearly 30 years. In 1703, finding his ever increasing activities too onerous, he resigned his professorship, to devote himself to his duties as Master of the Mint, to the scientific work of his contemporaries, and to defending his own work against the attacks of jealous rivals. In this same year, he was elected President of the Royal Society, an office to which he was reelected annually during the remaining 25 years of his life. In 1705, he was knighted by Queen Anne.

Most of Newton's important scientific work was done before he vacated the professorship in 1703, although he remained thereafter "a power of the first magnitude in the world of science." In his later years, he devoted much time to theological studies, particularly questions of Biblical criticism and chronology. He died Mar. 20, 1727, at the ripe old age of eighty-five. Throughout his life, he shunned publicity and

retained a modesty and simplicity which is indicated by a sentiment uttered shortly before his death:

> I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the seashore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

Any brief account of Newton's work must inevitably give a very inadequate impression of his contributions to science. The student is urged to read some of his writings first hand or, at least, some extensive biographical discussion of his life and work. We can here refer only to a very few of his researches on optics and on mechanics.

Newton's work on optics arose out of an attempt to improve lenses. The lenses made by Galileo and his immediate successors all had spherical surfaces. Optical instruments made with such lenses showed increasingly indistinct images as the powers of those instruments were increased. And there seemed to be an upper limit to the power of telescopes consistent with good definition.

The inability of a lens with spherical surfaces to bring parallel rays to a point focus was early recognized. In 1629, Descartes had shown that lenses with hyperbolic or, under certain conditions, parabolic surfaces should be free from the defect which we now call "spherical aberration"; and many schemes were proposed for grinding lenses with such surfaces. Newton found, however, that such lenses produced only a very slight improvement in the image, and he conjectured that, perhaps, the trouble lay not in the lens but in the light itself.

Accordingly, he procured a prism of glass and, placing it over a hole $\frac{1}{4}$ inch in diameter, through which sunlight was shining into a darkened room, he observed the "very vivid and intense colors" produced on a wall some 20 feet distant. Newton was surprised to find that this "spectrum," as we now call it, was so much longer than it was wide ($13\frac{1}{4}$ by $2\frac{5}{8}$ inches). The *width* subtended at the hole an angle (about 31 minutes) corresponding *exactly* to the sun's angular diameter. But the length—$13\frac{1}{4}$ inches—could not be so explained. Unaware of the true explanation, he made various surmises as to the origin of the colors, such as the varying thickness of the prism from apex to base, the unevenness of the glass, a curvilinear motion of the light after

leaving the prism, etc. One by one, experiment proved these hypotheses wrong.

Finally, he isolated one ray, or "color," after another, by suitable screens, and caused it to pass through a second prism. In this way, he could measure the refrangibility of each ray. And he found that the refrangibility increased from red to violet; that, therefore, the first prism simply "sorted out" the colors, which, in combination, made "white" light. In other words, so-called "white light" is made up of the spectral colors—a very elementary concept to us of the twentieth century but very new and of far-reaching importance in 1666.

Newton at once saw that this phenomenon, this dispersion of light, was the cause of his failure to effect any substantial improvement in telescopes by use of paraboloidal lenses. "Chromatic" aberration could not be eliminated by mere change of lens form.

Accordingly, he turned his attention to the reflecting type of telescope, one form of which had been described by James Gregory, in 1663. With his own hands, Newton made several small instruments, one of which was presented to the Royal Society in 1671. These telescopes do not seem to have been put to any important scientific use, and, as Newton made no more, the development of reflectors was dropped for 50 years.

Indeed, the development of *refracting* telescopes was retarded many years because of Newton's singular error in assuming, on the basis of a hurried experiment, that, in different media, dispersion was always proportional to refracting power. As noted above, the power of refracting telescopes had reached the upper limit set by chromatic aberration. And, in 1684, Newton declared "the improvement of telescopes by refraction to be desperate." Although, in the same year, Gregory had suggested that, in imitation of the human eye, the object glasses of telescopes might be composed of media of different density, yet Newton's incorrect assumption seemed to make achromatic telescopes an impossibility. And it was not until 1730, that Hall, by a suitable combination of crown and flint glasses made several achromatic combinations.

But Hall published no account of his work. Nearly 40 years later, the principle of the achromatic combination was rediscovered by Dolland, who, in 1758, presented to the Royal Society a paper on the dispersive powers of different substances. He

was, thus, led to try combinations of crown and flint glasses, with such success that, in spite of the previous work of Hall, Dolland was granted a patent on achromatic lenses—an invention within the grasp of Newton, three-quarters of a century before.

Newton's theories concerning the nature of light are of great historical interest. And much has been written concerning the extent to which he is supposed by some to have retarded the development of optics, by espousing the corpuscular theory as against the wave theory of his contemporaries, Huyghens (1629–1695) and Hook (1635–1703). Accordingly, it may be of interest to point out, by a quotation or two, that Newton, apparently, was by no means dogmatic in his support of the corpuscular theory and that later writers may have taken him, in this regard, more seriously than he intended.

In a communication to the Royal Society, in 1675, concerning "An Hypothesis Explaining the Properties of Light" Newton states:

> . . . I have here thought fit to send you a description . . . of this hypothesis . . . though I shall not assume either this or any other hypothesis, not thinking it necessary to concern myself whether the properties of light discovered by men be explained by this or any other hypothesis capable of explaining them; yet while I am describing this, I shall sometimes, to avoid circumlocutation . . . speak of it as if I assumed it.

He then proceeds to describe "an ætherial medium, much of the same constitution with air but far rarer, subtiler and more strongly elastic" but which vibrates "like air, only the vibrations [being] far more swift and minute." This "aether"

> . . . pervades the pores of crystal, glass, water and other natural bodies yet it stands at a greater degree of rarity in those pores than in the free ætherial spaces, and at so much a greater degree of rarity as the pores of the body are smaller.[1]

[1] That is, the ether is *less* dense in transparent bodies than in free space. Newton apparently makes this assumption by analogy with his erroneous conception of the cause of the rise of liquids in capillary tubes. He assumes this rise to be due to a reduced pressure of the *air* within the tube: the smaller the tube the higher the liquid rises, and therefore the "greater the rarity." The pores of transparent bodies must be *very* small. Hence, the attenuation of the ether within them must be very great.

He then supposes that

> . . . light is neither æther, nor its vibrating motion, but something of a different kind propagated from lucid bodies. They that will may suppose it an aggregate of various peripatetic qualities. Others may suppose it multitudes of unimaginable small and swift corpuscles of various sizes springing from shining bodies . . . and continually urged forward by a principle of motion which in the beginning accelerates them, till the resistance of the aetherial medium equals the force of that principle much after the manner that bodies let fall in water are accelerated till the resistance of the water equals the force of gravity.

Further, "light and æther mutually act upon one another, æther in refracting light and light in warming æther."

Refraction is accomplished in this wise: When a beam of light passes obliquely from, say, glass to air, it passes from *rare* ether to *denser* ether through a transition layer of increasing density. During the passage through this layer, the denser ether beyond, perhaps by repulsion, causes a "continual incurvation" of the beam of light toward the rarer ether; *i.e.*, the ray is "bent from the perpendicular," as we now say. The reverse occurs in passing from air to glass. Evidently, the light, whatever it is (!), should go more rapidly in glass than in the air.

> Just as bodies of various sizes . . . do by percussion excite sounds of various tones . . . so, when the rays of light, by impinging on the stiff refracting superficies, excite vibrations in the æther, those rays, *whatever they be*,[1] as they happen to differ in magnitude, strength, or vigour, excite vibrations of various bigness,

giving rise to a sense of color. This theory, as proposed by Newton, is a combination of the undulatory theory and the corpuscular theory.

Nearly 33 years later (1704), Newton published his optical researches in book form in his well-known "Opticks." The third edition of this appeared in 1721 and, without doubt, contains his mature judgment on the subject. The first sentence of this book reads: "My Design in this Book is not to explain the Properties of Light by Hypotheses, but to propose and prove them by Reason and Experiment." He then, in some 300 pages, gives his researches on refraction, reflection, colors of thin plates, etc., and he concludes the book by "proposing only some quèries

[1] The italics are the author's.

in order to further search to be made by others." Among these "queries" are the following:

1. Do not bodies act upon light at a distance, and by their action bend its rays . . . ?

5. Do not bodies and light act mutually upon one another, that is to say, bodies upon light in emitting, reflecting, refracting and inflecting[1] it; and light upon bodies for heating them, and putting their parts into a vibratory motion wherein heat consists?

12. Do not the rays of light in falling upon the bottom of the eye excite vibrations in the tunica retina; which vibrations, being propagated along the solid fibres of the optick nerves into the brain, cause the sense of seeing?

28. Are not all hypotheses erroneous in which light is supposed to consist in pression or motion propagated through a fluid medium? If light consists only in pression propagated without actual motion, it would not be able to agitate and heat the bodies which refract and reflect it, and . . . it would bend into the shadow. For pression or motion cannot be propagated in a fluid in right lines beyond an obstacle . . . but will bend and spread every way into the quiescent medium which lies beyond the obstacle.

29. Are not the rays of light very small bodies emitted from shining substances? For such bodies will pass through uniform mediums in right lines without bending into the shadow, which is the nature of rays of light . . . Pellucid substances act upon the rays of light at a distance in refracting, reflecting and inflecting them, and the rays mutually agitate the parts of those substances in heating them; and this action at a distance very much resembles an attractive force between bodies.

These quotations from Newton's "Queries" are illustrative of his speculations concerning the nature of light. That they are not intended as dogmatic assertions in the form of questions is indicated by the two following quotations which raise queries quite opposed to each other. In Query 18, after pointing out that a thermometer suspended in a vacuum in a cold room will, upon being transferred to the warm room, soon come to the temperature of the warm room, he says:

Is not the heat of the warm room convey'd through the vacuum by the vibrations of a much subtiler medium than air, which after the air was drawn out remained in the vacuum? And is not this medium the same with that medium by which light is refracted and reflected and by whose vibrations light communicates heat to bodies? . . . And do not hot bodies communicate their heat to contiguous cold ones by the

[1] That is, diffracting.

vibrations of this medium? . . . And doth it [the medium] not readily pervade all bodies? And is it not (by its elastick force) expanded through all the heavens?

Apparently, heat, but not light, might involve vibrations in this medium. But later on, in Query 28, after discussing the retardation of bodies moving through a fluid and pointing out that the motion of the planets is "regular and lasting," he says:

A dense fluid can be of no use for explaining the phaenomena of nature, the motions of the planets and comets being better explain'd without it. It serves only to disturb and retard the motions of those great bodies, and make the frame of nature languish: and in the pores of bodies it serves only to stop the vibrating motions of their parts, wherein their heat and activity consists. And as it is of no use, and hinders the operations of nature, and makes her languish, so there is no evidence for its existence and therefore it ought to be rejected. And if it be rejected the hypothesis that light consists in pression and motion propagated through such a medium is rejected with it.

Then follows Query 29, quoted above.

Apparently, Newton was frankly raising questions. For, in one of the concluding paragraphs of the books, he says:

In this third Book[1] I have only begun the analysis of what remains to be discovered about light and its effects upon the frame of nature, hinting several things about it and leaving the hints to be examined and improved by the farther experiments and observations of such as are inquisitive. And if natural philosophy in all its parts, by pursuing this method shall at length be perfected, the bounds of moral philosophy will also be enlarged.

But if Newton was only "leaving hints to be examined," he left some very profound ones. For, in Query 30, he asks:

30. Are not gross bodies and light convertible into one another, and may not bodies receive much of their activity from the particles of light which enter their composition? . . .

The changing of bodies into light and light into bodies, is very conformable to the course of nature which seems delighted with transmutations . . .

We begin, perhaps, to see an answer to this query in the modern doctrine of the equivalence of matter and radiant energy—a theory which accounts for solar and stellar radiation on the basis of an actual "transmutation" of matter. The very fact that Newton *raised* this question, particularly in such concrete form, is

[1] That is, the third section of the book on "Opticks."

an indication of the searching power of his intellect. And his willingness to leave the answer "to such as are inquisitive," who can base their conclusions on "farther experiments and observations" is abundant proof of his sound scientific judgment.

Newton's researches on optics alone would have given him a high rank, perhaps even premier place, among the scientists of his time. But of still greater value was his work in mechanics. In announcing that "every particle of matter in the universe attracts every other particle with a force inversely proportional to the square of the distance between the two particles"; in showing that this one universal and comparatively simple law governs not only the motions of the planets round the sun and of the satellites round their planets but, probably, also the relative motions of all the heavenly bodies, Newton gave to the world a truth the importance of which in all branches of human thought can hardly be overestimated. Of value to science, of course, from microphysics to macraphysics. But consider the effect on man's concept of nature and of his relations thereto of realizing—indeed, of having proven to him, for the first time—that the physical universe is governed by *law*, not by caprice; and if the *physical* universe, why not the biological universe, even the moral universe!

But how did Newton come to these discoveries? It is an interesting story.

Newton early appreciated the correct *quantitative* significance of the qualitative statements regarding motion, put forth by Galileo, and, as a result, he formulated the three *laws* of motion which bear his name. He was certainly familiar with Kepler's *quantitative* laws of planetary motion and, probably, also, with Kepler's speculations regarding gravitation as the cause of these motions. It remained to put this "power of gravity" in *quantitative* form. Accordingly, Newton attacked the problem of finding out a law of gravitational attraction between two bodies, as the sun and a planet, which would result in Kepler's third law, namely, that the squares of the periods of rotation of the planets round the sun are proportional to the cubes of their mean distances from the sun.

The gist of Newton's reasoning is as follows: Suppose the attraction between sun and planet to vary as the inverse xth power of the distance between them. That is, let

$$F_g = G\frac{Mm}{r^x}$$

where F_g is the force of attraction, G is some constant, M and m the mass of sun and planet, respectively, and r their distance apart. The centripetal[1] force F_c required to keep the planet in motion in its (nearly) circular orbit is

$$F_c = \frac{mv^2}{r}$$

where v is the speed of the planet in its orbit. Assuming the gravitational attraction to be the origin of the centripetal force, it follows that

$$G\frac{Mm}{r^2} = \frac{mv^2}{r}$$

And since, letting T equal the period of revolution,

$$v = \frac{2\pi r}{T}$$

we have

$$G\frac{Mm}{r^x} = \frac{4\pi^2 mr}{T^2}$$

This can, at once, be written in the form

$$\frac{T^2}{r^{x+1}} = \frac{4\pi^2}{GM}$$

For a given family of planets around a central body of mass M, T^2/r^{x+1} is, therefore, constant for the several planets and is independent of their masses. But Kepler's third law, based on *observation*, states that for the several planets T^2/r^3 is constant. It follows at once that

$$x = 2$$

and a gravitational attraction varying as the inverse square of the distance gives this third law of planetary motion.

Newton saw that a test of this inverse-square law could easily be made by comparing the acceleration of the moon toward the earth, with the acceleration of free falling bodies at the surface of the earth. He had shown that toward an external body a sphere acts as if all its mass were concentrated at its center. It was known that the distance between the moon and the earth's center is about sixty times the earth's radius. By the inverse-square law, therefore, the moon should "drop" toward the earth, in 1 second, $\frac{1}{60^2}$ as far as a body at the surface of the

[1] Both Newton and Huyghens were familiar with acceleration toward the center, of bodies moving in uniform circular motion. Newton's second law of motion at once gave the law of centripetal force.

earth drops in 1 (*i.e.*, the first) second. The latter distance being, from observations on falling bodies, 16 feet, the former should be $16/60^2$ feet, or 16 feet in 1 minute.

But the acceleration of the moon could be determined directly from the expression

$$a = \frac{v^2}{r}$$

$$= 4\pi^2 \frac{r}{T^2}$$

where T is the period of the moon's motion around the earth and r is the radius of the moon's orbit. Now, r is equal to sixty times the earth's radius, which was taken as 3,436 miles, on the then common assumption that a degree of latitude is 60 miles. On this basis, the moon is found to "drop" 13.9 feet toward the earth in a minute, instead of 16 feet, as should be the case if the inverse-square law were obeyed. The two results did not agree. Was the inverse-square law wrong?

Newton was twenty-three years old at the time, and he abandoned the work, not mentioning to anyone either his results or his disappointment. Some years later, he learned of a new and more accurate determination of the length of a degree which had been made by Picard, who found, not 60, but more nearly 70, miles. Newton, apparently in 1682, on the basis of Picard's new value for the length of a degree, revised his computations on the moon's acceleration and, to his great joy, found that it falls toward the earth 16 feet in a minute, just as predicted by the inverse-square law. At last, he had discovered the true law of gravitation. On the basis of this law, he could now *derive* all three of Kepler's laws. Theory and observation checked perfectly.

These results, together with some propositions on the motion of the planets, were communicated, in 1683, to the Royal Society, which requested permission to publish Newton's complete researches on the subject of motion and gravitation. Newton consented to prepare the material for publication, and, in 1687, appeared the first edition of the "Principia," or, in full, PHILOSOPHIAE NATURALIS PRINCIPIA MATHEMATICA (Mathematical Principles of Natural Philosophy) "without exception the most important work in natural philosophy extant."[1]

[1] HART: "Makers of Science."

The original is in Latin, but English translations are available. To these the reader is referred. The treatise is divided into three books, the subject matter of each being presented by propositions, theorems, and corollaries, the famous three laws of motion being assumed as axioms. The first two books deal with general theorems concerning the motions of bodies. For example, Proposition XI of Book I solves the problem:

> If a body revolves in an ellipse, it is required to find the law of the centripetal force tending to the focus of the ellipse.

The solution is the inverse-square law. Proposition LXXI proves, assuming the inverse-square law for small particles:

> . . . that a corpuscle placed without a [thin] spherical shell is attracted toward the center of the shell with a force reciprocally proportional to the square of its distance from that center.

Book III applies these general propositions to "demonstrate the frame of the System of the World." For example, Proposition VI states:

> . . . that all bodies gravitate towards every planet; and that the weights of bodies towards any (given) planet, at equal distances from the center of the planet are proportional to the quantities of matter which they [*i.e.*, the bodies] severally contain.

The entire treatise is characterized by the exposition of the Principle of Universal Gravitation and its ramifications, without, however, as Newton very carefully points out, attempting any hypotheses as to the *cause* of gravitation.

He says:

> To us it is enough that gravity really does exist, and acts according to laws which we have explained, and abundantly serves to account for all the motions of the celestial bodies and of our sea.

Of Newton's invention of the method of fluxions (*i.e.*, the calculus), of his very interesting miscellaneous writings, particularly those on theology, of the many controversies with his contemporaries into which he was unwillingly drawn in defense of his scientific work, we cannot take space to write. In urging our readers to make further study of the life and works of this renowned physicist, we may quote the words of his chief biographer, Sir David Brewster, who wrote:

The name of Sir Isaac Newton has by general consent been placed at the head of those great men who have been the ornaments of their species.

6. Newton's Contemporaries.—If we except the publication and revision of his scientific writings, the productive period of Newton's life ended about 1700. One finds his biography so full of interest and inspiration that one is tempted to discuss, similarly, the work of his contemporaries, themselves eminent scientists—the Honorable Robert Boyle (1627–1691), "saint and scientist," whose researches on the atmosphere have been immortalized by "Boyle's Law"; Huyghens (1629–1695), whose wave theory of light was to triumph a century and a half later over the corpuscular theory; Robert Hooke (1635–1703), proponent of the undulatory theory and originator of "Hooke's law" of elasticity; Leibnitz (1646–1716), whose calculus ultimately replaced Newton's fluxions. But, remembering that the main business of this book is *modern* physics, we must pass on to a rapid review of the developments of physics during the eighteenth century.

7. Mechanics[1] during the Eighteenth Century.—Newton's work had so thoroughly covered the fundamentals of mechanics, that, during the eighteenth century, there were no new discoveries of note. Rather, the period is characterized by the extension of the principles laid down by Newton and by their application to all sorts of problems. Among the prominent workers during the eighteenth century, we find such names as Daniel Bernoulli (1700–1782), who worked on hydrodynamics, the kinetic theory of gases, and the transverse vibrations of rods; Euler (1707–1783); Clairaut (1713–1765); D'Alambert (1717–1783); and Lagrange (1736–1813); all students of theoretical mechanics, whose researches paved the way for important advances made during the nineteenth century. One item of note is the invention, about 1780, of the Atwood's machine by George Atwood (1746–1807).

8. Heat during the Eighteenth Century.—Among the important advances in heat during the eighteenth century may be mentioned the development of thermometers and thermometric scales and the discovery and study of latent heats and specific

[1] The reader will find MACH's "The Science of Mechanics" very valuable in giving a correct historical perspective regarding the fundamentals of the subject.

heats. Galileo had invented the thermometer, in 1597, and had proposed a temperature scale, in 1613. The first mercury thermometer was used by Kircher, in 1643, but it is to Fahrenheit (1686–1736) that we owe the first reliable thermometers. About 1724, Fahrenheit proposed the temperature scale now known by his name. This was followed by the Reaumur scale, in 1734, and by the Celsuis scale, in 1742, all based on the fixed temperatures of melting ice and boiling water.

Discoveries in the field of latent and specific heats are due to James Black (1728–1799), Professor of Chemistry at Glasgow and Edinburgh. His measurements of the heat of fusion and of vaporization of water form the basis of modern calorimetry and gave definite form to the previously hazy distinctions between temperature and heat.

With regard to theories of heat, there was retrogression during the eighteenth century. From the quotations given above (pp. 40 and 41), it is clear that Newton regarded heat as intimately connected with the motion of the small particles of which bodies are composed. This view seems to have been shared by Newton's contemporaries. But early in the eighteenth century there was a return to the "materialistic" or "caloric" theory of heat, which held that heat is a subtle, highly elastic fluid which could be extracted from or added to a body, thereby causing the changes of its temperature. This heat fluid was indestructible, its particles were self-repellant but were attracted by ordinary matter, and it was all-pervading. The expansion of bodies when heated was the natural result of "swelling" due to forcing caloric into matter. The production of heat by percussion was due to the releasing or "pounding loose" of some of the caloric naturally condensed in or absorbed by the body, thereby increasing the amount of free caloric within the body. Black, whose experiments on calorimetry were mentioned above, explained latent heats and specific heats on the basis of this theory. Indeed, by the end of the eighteenth century, the materialistic theory of heat was quite generally accepted.

9. Light during the Eighteenth Century.—Reference has already been made (p. 37) to the development of achromatic lenses by Hall and, later, by Dolland. This discovery paved the way for substantial improvements in refracting telescopes, but the impossibility of getting larger pieces of flint glass of good optical quality set an unfortunate upper limit to the size of

refractors. And, consequently, astronomers turned their attention to reflectors for telescopes of large light-gathering power. Especially noteworthy are the telescopes made by William Herschel (1738–1822), the largest one being 4 feet in diameter. Herschel's skill in constructing these instruments was surpassed by his skill and diligence in using them. He discovered the planet Uranus and two of its satellites, two satellites of Saturn, a very large number of nebulæ and double stars, the motion of the solar system through space—indeed, he established a new standard of observational astronomy. He did for the solar system what Copernicus, Kepler, and Tycho had done for the earth. They gave the earth its proper place among the planets. He gave the solar system its proper place among the stars.

An event of extraordinary importance in the history of sciences was the discovery of the aberration of light, by Bradley, in 1728. The absence of any measurable stellar parallax was one of the stumbling blocks in the way of the Copernican system and, therefore, was one of the outstanding problems of astronomy. Tycho recognized that, viewed from opposite sides of the earth's orbit, the stars should show a perspective displacement. His careful observations convinced him that no such displacement so great as 1 minute of arc existed. Later observers, likewise, sought in vain.

Meantime, in 1675, Römer, a Danish astronomer, by a systematic study of the eclipses of Jupiter's moons as they pass behind that planet, had found that the interval between eclipses was longer when the earth was receding from Jupiter and shorter when the earth was approaching Jupiter. When the earth is on the opposite side of the sun from Jupiter, Römer found that the eclipses were some 22 minutes[1] behind schedule, as compared with the occurrence of the eclipses when the earth and Jupiter are on the same side of the sun. Römer correctly explained this discrepancy by assuming that it takes light 22 minutes to cross the earth's orbit. From an approximate knowledge of the diameter of the orbit, he computed that the velocity of light must be about 190,000 miles per second. This was the first determination of the velocity of light.

In hopes of being able to measure stellar distances, Bradley (1692–1762), in December, 1725, began systematic observations on the position of a zenith star, γ Draconis. If stellar parallax

[1] The modern value is about 16½ minutes.

existed, this star should be farthest south in December and should then move north, reaching its maximum northerly position 6 months later. The position of the star was found to change, but not in the manner expected. It reached farthest south in *March* and farthest north in *September*, the angular distance between the two positions being about 40 seconds of arc. Bradley continued his observations with a larger instrument and on other stars, and, in 1728, he came to the conclusion that the observed displacement was not due to parallax at all but to an apparent shift in the star's position due to a combination of the velocity of light with that of the earth in its orbit.[1] He was, thus, enabled to deduce a value for the velocity of light which was in substantial agreement with that determined by Römer a half-century earlier. This discovery of Bradley's was the first in the series which eventually led to the theory of relativity.

Theories as to the nature of light made no material progress during the eighteenth century. Some writers are inclined to ascribe this to the prestige given to the corpuscular theory by the fact that it was supported by Newton, whose preeminence "seemed to act like a spell," as had Aristotle's, centuries before. But if so, then, likewise, the dynamic theory of heat held by Newton should have been uppermost during the eighteenth century, whereas, as has already been pointed out, the reigning theory of heat during this period was the caloric theory. Lack of progress in the theory of light was, of course, due to lack of any crucial experiment, just as was the case with theories of heat. Science has never progressed on the basis of speculation only.

10. Electricity during the Eighteenth Century.—With the possible exception of theoretical mechanics, electricity received more attention during the eighteenth century than did any other branch of physics. But until the discovery of electric currents, at the end of the century, research was concerned with electrostatics.

Stephen Gray (1670–1736) discovered that the difference between conductors and non-conductors of electricity depends on the material, and he showed that conducting bodies may be electrified by insulating them. Du Fay (1698–1739) extended Gray's experiments and showed that all bodies may be electrified;

[1] See any text on astronomy for further explanation of the cause of the phenomenon.

that flames exercise a discharging power; and that there are two kinds of electricity which he called "vitreous" and "resinous." He was, thus, led to propose the two-fluid theory of electricity to explain attraction and repulsion. During the first half of the eighteenth century, the electroscope was invented (by Hawksbee, in 1705), frictional electric machines were developed, the leyden jar discovered (1745), and there was considerable popular interest in electrical phenomena.

During the latter half of the century, three names stand out preeminent: Benjamin Franklin (1706–1790), Henry Cavendish (1731–1810), and Charles A. Coulomb (1736–1806).

Franklin's experiments began about 1745. One of his first observations was the effect of points "in drawing off and throwing off the electrical fire." He proposed the one-fluid theory of electricity, somewhat similar to the caloric theory of heat. This theory supposed that all bodies naturally contain a certain amount of this fluid. When a body had an excess of the fluid, it was "plus," or positively, electrified. When it had a deficit, it was "minus," or negatively, electrified. In form, this theory is similar to our present electron theory of electrification, with signs changed. But the Franklin theory can hardly be called the forerunner of our modern theory, which grew out of experiments of a very different kind.

About 1750, Franklin began to speculate on the identity of electricity and lightning, pointing out many similarities and proposing, by means of a pointed iron rod, to "draw off the fire from a cloud." Franklin's writings were published in Europe, and, in 1752, Dalibard actually tried the experiment in Paris, confirming Franklin's prediction. A short time later, Franklin, to verify Dalibard's results, performed the famous kite experiment, so well known to every schoolboy. This led to his study of atmospheric electricity and to his invention of the lightning rod. Franklin's researches occupied but a small portion of his long and busy life, but they were sufficient to give him a high standing among the scientists of the world.

Up to and including Franklin's work, studies of electrostatics had been qualitative. Then came the *quantitative* researches of Cavendish and of Coulomb.

Cavendish is known not only for his work in electrostatics but also for his researches in chemistry and for the well-known "Cavendish experiment," in 1798, in which he determined the

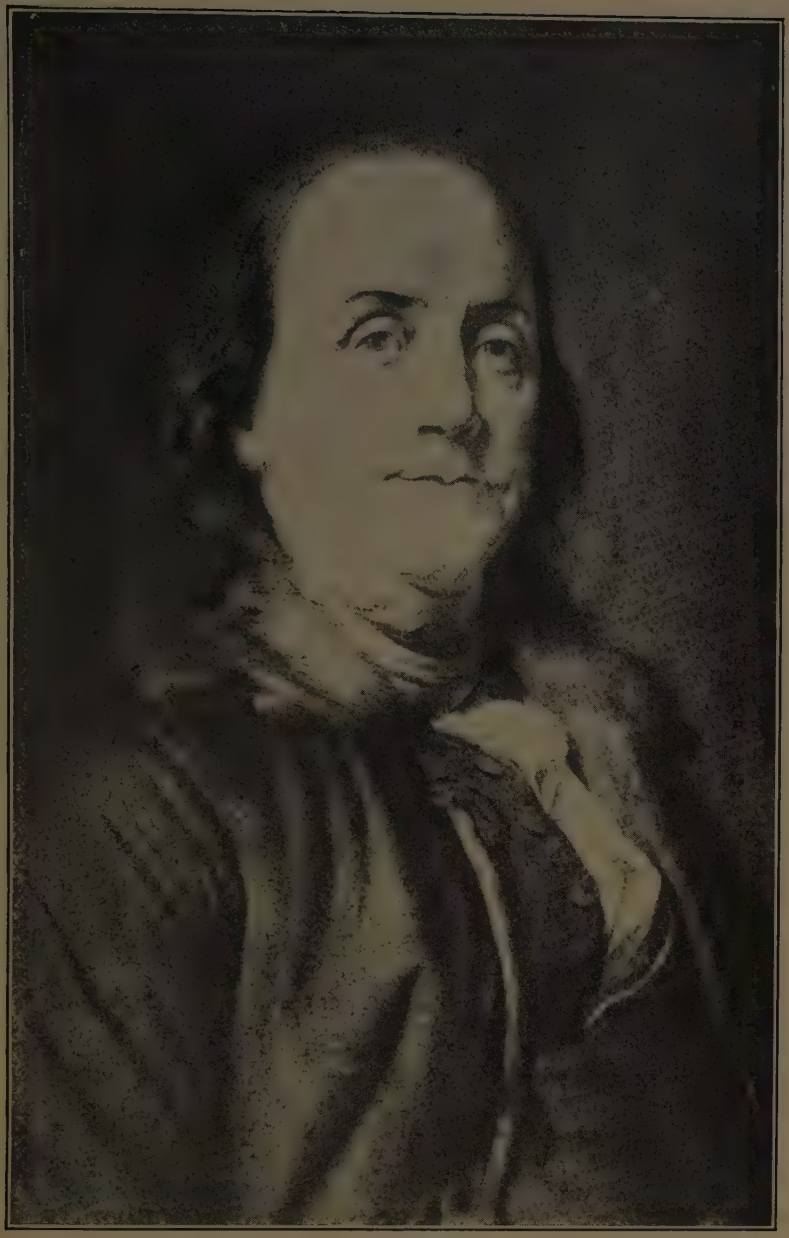

PLATE 4.—Franklin.

(*Facing page* 50)

constant of gravitation. His electrical researches were very extensive and covered the period from about 1770–1780, but most of his work remained unknown, for he published only one paper of importance: "An Attempt to Explain Some of the Principal Phænomena of Electricity by Means of an Elastic Fluid." This appeared in the Philosophical Transactions of the Royal Society in 1771. He left behind a large amount of material, however, in the form of manuscript notes. These were edited and published, in 1879, by Maxwell, under the title "The Electrical Researches of the Honorable Henry Cavendish, F.R.S." In these experiments, Cavendish proved the inverse-square law of electrostatic force; measured capacity and expressed it correctly in "inches;"[1] recognized the principle of the condenser and measured the specific inductive capacity of several substances; had a reasonably clear idea of the quantity which we now call "potential"; and anticipated Ohm's law by 50 years. His measurements were made by means of an electrometer of the pith-ball type, the balls being "made of pith of elder, turned round in a lathe, about one-fifth of an inch in diameter and suspended by the finest linen threads that could be procured, about 9 inches long." Later, he used "a more exact kind of electrometer" consisting of cork balls suspended by gilt-covered wheat straws. Had these important measurements been communicated to his scientific contemporaries, the history of electricity might have been substantially modified. Maxwell quotes Franklin as saying of Cavendish: "It were to be wished that this noble philosopher would communicate more of his experiments to the world, as he makes many, and with great accuracy."

Coulomb's work in electricity grew out of his development of the torsion balance, originally used for studying the torsional elasticity of wires. In the period 1785–1789, he published seven papers on electricity and magnetism in the *Memoirs de l'Academie Royale des Sciences*. In these papers, he showed, by means of the torsion balance, that electrostatic forces obey the inverse-square law; that on conducting bodies, the charge exists only on the surface; and that the capacity of a body is independent of the nature of the material of which it is composed. Most of

[1] Cavendish's unit was one-half the modern unit, since he used the *diameter* of the sphere instead of its radius. His standard of capacity was a sphere 12.1 inches in diameter.

Coulomb's discoveries had been anticipated by Cavendish, but, on account of the latter's failure to publish his work, the former's experiments were taken as the basis of theoretical studies by Poisson and others. Coulomb advocated the two-fluid theory of electricity.

This second period comes to a close with rival theories contending in each of three of the subdivisions of Physics: the caloric *vs.* the dynamic theory in heat; the corpuscular *vs.* the undulatory theory in light; and the one-fluid *vs.* the two-fluid theory in electricity. The very fact that these issues were raised, in rather clean-cut fashion, is an indication of the tremendous strides which had been taken since Galileo. But most important of all, men had learned the value of experiment and observation and the fallacy of blindly following "authority." Physics was ready to profit by the discoveries about to be made by Rumford, Davy, Young, Oersted, and Faraday.

CHAPTER III

HISTORICAL SKETCH, THIRD PERIOD (1800–1890 A.D.): THE RISE OF CLASSICAL PHYSICS

1. Heat and Energy.—The law of the conservation of energy is one of the most fundamental and far-reaching of all our physical laws, and yet, curiously enough, it is of comparatively recent origin, for it was not announced until the middle of the nineteenth century. It began in *qualitative* form with the experiments of Rumford, in 1798, and assumed its final and *quantitative* form after the experiments of Joule, about 1847.

Rumford's[1] work marks the beginning of the end of the caloric theory of heat. About 1798, while engaged in boring out some cannon for the Bavarian government, he was impressed with the large quantity of heat produced. What was its source? If the caloric theory were correct, then this great evolution of heat ought to result in a loss of "something," perhaps weight, by the gun, the chips, or the tool. But no such loss could be observed. Perhaps the caloric theory, so generally accepted at that time, was wrong! If so, an *experiment* should answer the question.

Accordingly, by a mechanism worked by two horses, he caused a blunt steel boring tool to rotate, under great pressure, on a piece of brass, the brass and tool being immersed in water. In 2 hours, the water actually boiled. Apparently, heat would be produced by this apparatus just as long as the horses kept

[1] Count Rumford, or, as he was originally known, Benjamin Thompson, was born in New England in 1753. He appears to have exhibited, very early, a taste for science. When the War of the Revolution broke out in 1775, he took sides with the British and fled to England, leaving behind him in America his wife and child whom he never saw again. In 1778 he was made a Fellow of the Royal Society. He left England in 1783 and became a sort of military engineer to the Bavarian government, which conferred on him the title "Count Rumford." It was in this capacity, in 1798, that he performed the experiment of producing heat by friction. It is also of interest to note that, in 1800, he founded the Royal Institution in London, which, for a century and a quarter has been one of the leading scientific institutions of the world. He died in France in 1814.

going, the quantity of heat which might, in this way, be generated being independent of the properties of the brass or the iron. But this conclusion, arrived at *by experiment*, was quite contrary to the caloric theory, according to which there should be a *finite* quantity of heat fluid in any body. Therefore, Rumford reasoned:

> . . . anything which any isolated body, or system of bodies, can continue to furnish without limitation cannot possibly be a material substance; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner heat was excited and communicated in these experiments, except it be motion.[1]

Rumford's conclusions—that heat results from motion—were so revolutionary and so contrary to the prevailing caloric theory, that they made but few converts. Sir Humphrey Davy, Director of the Royal Institution, was sufficiently impressed to experiment further. He observed that two pieces of ice, kept below the melting point, could be melted by rubbing them together, even if the experiment were performed in vacuum, but it was not until 1812 that he was convinced that the "cause of the phenomenon of heat is motion." Another convert was Thomas Young, who, in 1807, espoused the kinetic theory on the basis of Rumford's experiments.

But the majority of the supporters of the caloric theory were unconvinced. Even Carnot (1796–1832), the founder of the modern science of thermodynamics, when, in 1824, he proposed the now famous Carnot's cycle, based his reasoning on the caloric theory. A given quantity of caloric "falling" from a higher to a lower temperature was analogous to a given quantity of water falling from a higher to a lower level. Each was capable of producing motive power. The kinetic theory had to wait for a *quantitative* experiment or statement.

In 1842, R. J. Mayer (1814–1878) published a paper[2] in which, partly on philosophical grounds, he announced the equivalence of heat and energy and, from data on the specific heat of a gas at constant volume and constant pressure, he deduced a value for the mechanical equivalent of heat.

[1] Rumford's paper appeared in the Philosophical Transactions of the Royal Society for 1798.

[2] *Ann. der Chemie und Pharmacie*, May, 1842.

Meanwhile, Joule (1818–1889), in England, unacquainted with Mayer's work, was carrying on a very careful series of experiments, begun in 1840, in which he converted the mechanical energy of a falling weight into heat by a paddle wheel revolving in water and, thus, determined that 778 foot-pounds of work would raise 1 pound of water 1°F. Joule announced his results at a meeting of the British Association for the Advancement of Science, in June, 1847. The paper would have passed almost unnoticed, had it not been for William Thompson, later Lord Kelvin, who, grasping the real significance of the proposed theory, by his discussion made the paper the event of the meeting.

Quite independently of the work of Mayer and of Joule, Helmholtz (1821–1894), in 1847, read a paper before the Physical Society, in Berlin, on "Die Erhaltungen der Kraft," in which, on the basis of the impossibility of perpetual-motion machines, he announced the law of the conservation of energy. The paper was rejected for publication by the editor of the *Annalen der Physik!* It was later published in pamplet form.

The caloric theory could not withstand these attacks, and, by 1850, the mechanical theory of heat and the doctrine of energy and of the conservation of energy were, quite generally, accepted. After half a century, Rumford's theory had come into its own. *Heat was simply one of the several forms of energy.*

Upon this solid foundation, the science of heat grew apace, during the next 50 years. In part, under the impetus of applied science, there was accumulated a vast amount of data on the thermal properties of solids, liquids, vapors, and gases. Thermometry was put on a rational basis by Lord Kelvin's thermodynamic temperature scale. Thermodynamics itself became almost a separate science. The atomic and molecular theory of matter, combined with the kinetic theory of gases, all but made visible the actual motions which constitute thermal agitation. Indeed, the theory of heat and energy, the "classical theory," as we now call it, with all its ramifications in the various branches of both pure and applied science, seemed to have reached its final form.

But, in the closing years of the nineteenth century, a careful study of the phenomena of radiation established experimental laws which the classical theory could not explain. Either a new theory or a modification of the existing one was necessary. The latter alternative led to the development of the quantum

theory, which left a large part of the main structure of the classical theory intact, but which evolved radically new concepts to explain the new facts.

2. Light.—The revival of the wave theory of light, by Thomas Young (1773–1829), is one of the most important events in the history of the early years of the nineteenth century. It will be remembered that, since the time of Newton, the majority of scientists had supported the corpuscular theory. In 1800, Young published a paper in the *Philosophical Transactions* of the Royal Society under the title "Outlines of Experiments and Inquiries respecting Sound and Light," in which he pointed out (1) that the observed fact that the velocity of light is quite independent of the nature of the source—be this electric spark, a faintly glowing body, or the sun—is very difficult to explain on any corpuscular theory but follows, naturally, from the wave theory, since, by analogy with sound, the velocity of the light waves in the ether should be independent of intensity or frequency;[1] and (2) that the dividing of a beam of light into a refracted and a reflected ray at the interface between two media was to be expected from the wave theory but had not been satisfactorily explained by the adherents of the corpuscular theory.

A year later, Young presented to the Royal Society a paper "On the Theory of Light and Colors," in which he proposed the principle of the interference of two wave trains as an explanation of Newton's rings and the colors of thin plates. From Newton's careful measurements of the thickness of the air layers necessary to produce the several colors, Young was enabled to compute wave lengths. He found the wave length of yellow light, for example, to be 0.0000227 inches, a value in excellent agreement with modern data. In subsequent papers, he described the interference fringes which he had observed by placing hairs or silk threads in front of a narrow slit illuminated from the rear; he announced the change of phase on reflection; he explained diffraction bands by the principle of interference, and he showed that the spacing of these bands gave values of the wave length agreeing with those obtained from Newton's rings and that,

[1] It is a very curious circumstance that, a century later, an argument of a very similar kind proved to be a very serious embarrassment to the wave theory. For it was observed that the velocity with which photoelectrons are emitted under the influence of light is independent of the *intensity* of the source (but depends on the wave length). See p. 169.

therefore, both phenomena must be due to a common cause. Again, *quantitative* measurements became an indispensable link in the chain of reasoning.

But Young's paper aroused a storm of protest, even of derision and abuse. He had dared to question Newton's corpuscular theory! He was attacked not by the Church, as was Galileo, but by some of his scientific, or, more probably, pseudoscientific, contemporaries. His chief assailant was Henry Brougham, afterward Lord Chancellor of England, who "reviewed" Young's papers in the *Edinburgh Review*. The nature of Brougham's attack is indicated by the following quotations, taken almost at random:

> This paper [*i.e.*, Young's] contains nothing which deserves the name either of experiment or discovery . . .
>
> We wish to raise our feeble voice against innovations that can have no other effect than to check the progress of science, and renew all those wild phantoms of the imagination which Bacon and Newton put to flight from her temple. We wish to recall philosophers to the strict and severe methods of investigation . . .
>
> We . . . have searched without success for some trace of learning, acuteness and ingenuity, that might compensate his evident deficiency in the powers of solid thinking, calm and patient investigation, and successful development of the laws of nature by steady and modest observation of her operations.

Young was accused of deliberately misquoting other investigators and of many other "scientific" crimes.

Brougham's attacks, as full of abuse as they were devoid of science, were so evidently based on personal spite that they should have convinced no one. But though Young replied at length in a privately published pamphlet, it was a long time before public opinion was willing to receive his theories with an open mind. Young's final vindication came through the work of two Frenchmen, Fresnel and Arago.

The phenomenon of the polarization of light by Iceland spar had been discovered by Bartholinus, in 1669. Newton had tried to fit the corpuscular theory to polarization by assuming a sort of structure to the corpuscles. But the explanation was not convincing, and, indeed, polarization had proved an enigma to both theories of light.

In 1808, Malus (1775–1812), almost by accident, discovered the phenomenon of polarization by reflection. A year later, as a

result of further research, he announced the law of polarization which bears his name: *If a beam of plane-polarized light be incident onto a crystal of Iceland spar so that its plane of polarization makes an angle α with the principal plane of the crystal, the intensity of the ordinary ray transmitted by the crystal is proportional to $\cos^2 \alpha$; and of the extraordinary ray, to $\sin^2 \alpha$.*

A little later, Fresnel (1788–1827), unaware of Young's work, rediscovered the phenomenon of interference and performed the famous experiment with the two mirrors. His confidence in the wave theory as an explanation of the phenomenon was strengthened upon learning from Arago of Young's discoveries more than a decade earlier. But the difficulties of explaining polarization were as great as ever.

Finally, Young, in a letter to Arago, written in January, 1817, made the bold suggestion that all the phenomena of polarization could be explained on the assumption that the light vibrations were *transverse* rather than longitudinal. Quite independently, Fresnel reached the same conclusion. Subsequent experiments were in entire agreement with this assumption. For example, Fresnel and Arago showed that two plane-polarized beams of light could be made to interfere if their planes of polarization were parallel, but no interference was observed if the beams were polarized at right angles to each other. It had been difficult enough for scientists and philosophers to conceive of a *fluid* ether filling all space and transmitting *longitudinal* vibrations. But now they were asked to believe the still more impossible—that this medium, the ether, was a solid or, at least, had such of the properties of a solid as are necessary for the transmission of transverse waves, *i.e.*, the properties of rigidity and density. And yet the planets must still move through this "solid," pervading all space, with no measurable changes in their periods of revolution. No wonder the scientific public was even more incredulous!

Nevertheless, the *indisputable experimental evidence* of interference phenomena forced the conclusion[1] that light is a wave

[1] A close parallel to this situation is to be found in the origin, a century later, of Rutherford's nuclear theory of the atom, based upon the experiments of the scattering of alpha particles, a theory which was at once accepted, in spite of the fact that it seemed to necessitate the abandonment, or radical revision, of some of the fundamental concepts of electrodynamics (see Chap. X, Sec. 4).

motion, and the equally unambiguous evidence from experiments on polarization required that this wave motion be transverse. There seemed to be no escape from these conclusions.

But the crucial experiment was not performed until Foucault (1819–1868) measured the relative velocities of light in water and in air. It had been generally accepted that, on the basis of the corpuscular theory, the velocity of light should be greater the greater the optical density of the medium;[1] while the reverse should be the case with the undulatory theory. And it had been known for a long time that a determination of the relative velocities of light in air and in some optically denser medium, such as water, would decide between the two theories. But it was not until 1850, that experimental methods had developed to the point of making such a test feasible. In that year, Fizeau and Foucault, in part, independently, by means of the well-known, rotating-mirror method[2] previously proposed by Arago, ascertained that light travels more slowly in water than in air—a final triumph, so it seemed, for the wave theory.

Meantime, other evidence had been accumulating. Fraunhofer, in 1817, observed the dark lines in the solar spectrum. About 1820, he made excellent determinations of the wave length of the D-lines of sodium, by means of a grating made of fine wires. Babinet, in 1829, proposed the wave length of light as a standard of length. The phenomenon of dispersion was explained, on the basis of the elastic-solid theory of the ether, by Cauchy, who proposed his famous dispersion formula. In fact, the new wave theory seemed capable of explaining all optical phenomena.

From 1850, until the end of the third period (1890), the wave theory held the field, undisputed. Each new discovery seemed to strengthen its position. The frequent assertions that the corpuscular theory was finally disposed of certainly seemed justified, particularly after the development of Maxwell's electromagnetic theory of light and its experimental verification. But the corpuscular theory was not dead. It was only sleeping.

Some important discoveries in light from 1800 to 1890 not previously mentioned are:

[1] See EDSER: "Light for Students."

[2] See any textbook on optics.

	DISCOVERER
Three-color theory of vision (1807)	Young
Heat and light rays differ only in wave length (1807)	Young
Rotary polarization of quartz (1811)	Arago
Polarization of scattered light (1813)	Arago
Rotary polarization by liquids (1815)	Biot
Light sensitivity of silver bromide (1826)	Balard
Change of conductivity of selenium on illumination (1837)	Knox
Doppler effect (1842)	Doppler
Beer's law of absorption (1852)	Beer
Foundation of spectral analysis (1859)	Kirchhoff and Bunsen

3. Electricity and Magnetism.—The history of electricity during the nineteenth century is so extensive that even a sketchy outline would fill a small volume. We shall, therefore, discuss only a few of the more important events, particularly the works of Faraday, Henry and Maxwell. In singling out these three names for special biographical mention, there is no attempt to minimize the great contributions of their contemporaries—such men as Ampère (1775–1836), Oersted (1777–1851), Ohm (1787–1854), Wheatstone (1802–1878), Lenz (1804–1865), Stokes (1819–1903), Lord Kelvin (1824–1908), Kirchhoff (1824–1887), Tait (1831–1901), Hertz (1857–1894), and many others, whose names are intimately associated with theoretical and experimental electricity. But the work of Faraday and that of Maxwell are so closely related to each other and to the whole subject of modern physics that we can best present that part of electricity and magnetism in which we are particularly interested by giving an account of the contributions of these two men.

4. Michael Faraday.[1] (*a*) *Biographical Sketch.*—Michael Faraday was born Sept. 22, 1791, in a small village near London. He was the son of a blacksmith, James Faraday, who died in 1810, following a long illness. After a very rudimentary education, young Michael, to assist his mother in providing for the family, was engaged as errand boy to a bookseller and stationer, in 1804. He performed his duties so conscientiously that, in the following year, he was formally apprenticed to his employer to learn the art of bookbinding.

During this apprenticeship, Faraday made good use of his spare time by reading some of the books which passed through the shop. He was particularly interested in works on science, such

[1] See THOMPSON, SYLVANUS P.: "Michael Faraday: His Life and Work."

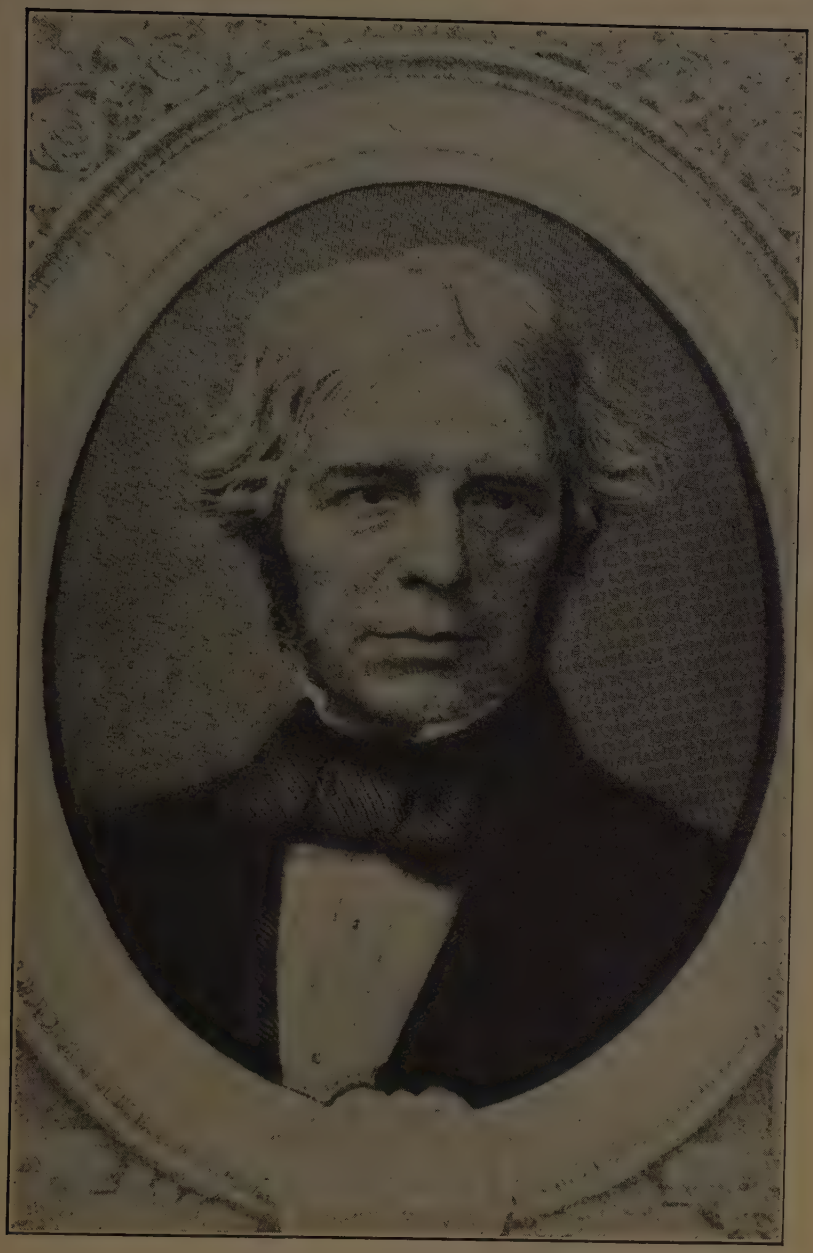

PLATE 5.—Faraday.

(*Facing page* 60)

as the articles on electricity in the "Encyclopedia Britannica" and in Marcet's "Conversations in Chemistry." In connection with the reading of the latter book, he showed one of the important characteristics[1] of the great investigator-to-be by performing such of the simple experiments described "as could be defrayed in their expense by a few pence per week." He also made some simple electrical apparatus.

Aside from his own reading, *Faraday's only scientific education consisted in a dozen lectures on natural philosophy by a Mr. Tatum, in the years* 1810 *and* 1811, *and four lectures on chemistry by Sir Humphrey Davy, in the winter of* 1812. The very careful and neatly written notes which he made of these lectures served him a very useful purpose when, after having finished his apprenticeship and being quite unhappy at his trade of bookbinder, he made bold to apply to Sir Humphrey Davy for a position, however menial, at the Royal Institution of which Davy was then director. "As proof of his earnestness" Faraday sent along with his application the notes which he had taken of Davy's four lectures. Davy was so pleased with the letter and the notes, that, eventually, in March, 1813, Faraday was engaged as apparatus and lecture assistant at 25 shillings per week.

In October, 1813, Faraday accompanied Sir Humphrey and Lady Davy on a trip to the Continent. During their 18 months' absence, they visited many of the important scientific centers of Europe and saw many of the continental scientists and something of their methods. Naturally, Faraday was much impressed and edified by what he saw and learned, but, assistant though he was, he also *left* an impression because of his modesty, amiability, and intelligence. Said one writer, "We admired Davy; we *loved* Faraday."

On returning to England, in the spring of 1815, Faraday was reengaged at the Royal Institution, at 30 shillings per week. At first, he simply "assisted," but, under the encouragement of Davy, he soon began original investigations, initially in chemistry. In 1816, he published his first paper, on "An Analysis of Caustic Lime." In 1817, he published 6 papers; in 1818, 11; and, in 1819, 19! These papers were concerned with such subjects as the escape of gases through capillary tubes; the production of sound in tubes by flames; the combustion of the

[1] In later life, he wrote: "I was never able to make a fact my own without seeing it."

diamond; and the separation of manganese from iron. About 1820, he began his electrical researches. These, and others growing out of them, continued for nearly 40 years.

Almost his entire scientific life was spent at the Royal Institution. In 1825, he was made Director of the Laboratory. Declining offers of positions elsewhere, turning away professional occupations which might have made him wealthy, he gave to his science and to the institution which he served a devotion seldom if ever equaled. The secret of his success, which brought him, during his lifetime, honors from all over the scientific world and which immortalized his name by the long list of scientific discoveries ascribed to him, is, perhaps, to be found in some excerpts from his many notes:

> Aim at high things, but not presumptuously.
>
> Endeavor to succeed—expect not to succeed.
>
> It puzzles me greatly to know what makes the successful philosopher. Is it industry and perseverance with a moderate proportion of good sense and intelligence? Is not a modest assurance or earnestness a requisite? Do not many fail because they look rather to the renown to be acquired than to the pure acquisition of knowledge . . . ? I am sure I have seen many who would have been good and successful pursuers of science, and have gained themselves a high name, but that it was the name and the reward they were always looking forward to—the reward of the world's praise. In such there is always a shade of envy or regret over their minds and I cannot imagine a man making discoveries in science under these feelings.

The reader is urged to study carefully Faraday's life and works, particularly to read, as unexcelled examples of scientific expositions, portions of his "Experimental Researches in Electricity and Magnetism."

Faraday's last scientific work was done about 1860. He died in 1867.

(*b*) *Earlier Work in Electricity and Magnetism.*—It is necessary to preface an account of Faraday's researches in electricity and magnetism by an account of the development of "current" electricity up to 1820. It will be remembered that all work in electricity up to about 1790 was confined to electrostatics. About that time, Galvani (1737–1798), as a result of a chance observation that a frog's leg kicked convulsively when connected with the terminal of an electric machine, was led to an extensive study of "animal electricity." In the course of these experi-

ments, Galvani observed that if the frog's leg were so suspended that the exposed nerves touched a metal plate, say silver, then, a contraction of the muscle occurred whenever the foot touched another metal, say iron. He even observed slight muscular contraction when both plates were of the same kind of metal. This led him to believe that the nerve was the source of electricity and that the metal served simply as conductor.

Volta (1745–1827) continued and extended Galvani's experiments and proved that the phenomenon was due to electricity generated by contact of dissimilar metals, and, in March, 1800, he communicated to the Royal Society a description of the first battery for producing an electric current—the historically famous Volta, or voltaic, "pile," consisting of zinc and copper plates placed alternately and separated by blotting paper moistened with brine. He also described the first voltaic battery, which consisted of cups containing brine or dilute acid connected by copper and zinc strips joined together.

This new source of electricity was received with a great deal of interest, and many important discoveries soon followed. Only a few weeks after Volta's communication, Nicholson and Carlisle (in May, 1800) accidentally discovered the decomposition of water by the electric current. Thinking to secure better contact between two wires forming part of the circuit, they joined the ends of the wires by a drop of water and, at once, observed the formation of a gas which they recognized as hydrogen. In September, 1800, Ritter observed the decomposition of copper sulphate, and, about the same time, Cruikshank showed that many solutions of salts could be similarly decomposed. In 1802, Davy discovered that the electrolysis of water yielded 2 volumes of hydrogen to 1 of oxygen. In the same year, Ritter discovered the principle of the storage battery. Sodium and potassium were discovered by Davy, by electrolysis, in 1807. During this same period were discovered the heating effect of the current, and the arc light.

It was early suspected that there was some relation between electricity and magnetism, and, indeed, a few scattered observations had been made, such as the magnetism of steel needles by lightning discharges. But the *science* of electromagnetism dates, quite definitely, from the discovery, in 1820, by Oersted (1777–1851), that a magnetic needle tends to set itself at right angles to a wire through which an electric current is flowing.

Immediately, the brilliant French physicist, Ampère (1775–1836), extended Oersted's discoveries; announced the well-known "Ampère's rule" for the relative direction of current flow and direction of deflection; discovered the mutual force action of two parallel currents on each other; invented the electromagnet; and made the first suggestions of the electric telegraph.

(*c*) *Faraday's Discovery of the Principle of the Motor.*—Faraday's interest in electromagnetism dates from April, 1821, when Wollaston attempted, at the Royal Institution, to make a wire carrying an electric current revolve around its own axis when the pole of a magnet was brought near. The experiment was unsuccessful, but the phenomenon excited Faraday's interest, and he determined to make a study of it. First, he read what had been done by others and repeated many of their experiments. In the course of these experiments, he observed that when the magnetic pole was brought near the wire, "the effort of the wire is always to pass off at right angles from the pole, indeed to go in a circle around it . . ."[1]

The following day, Sept. 4, he wrote:

> Apparatus for revolution of wire and magnet. A deep basin with a bit of wax at bottom and then filled with mercury. A magnet stuck upright in wax so that pole [is] just above surface of mercury. Then piece of wire, floated by cork, at lower end dipping into mercury and above into silver cup.

On passing a current through the wire, it revolved *continuously* around the magnet. This was the first electric motor! On Christmas Day, 1821, Faraday succeeded in making a wire carrying a current move under the influence of the earth's field.

It was decades before electric motors were to be built, but this experiment of Faraday's clearly sets forth the fundamental principle involved.

(*d*) *Electromagnetic Induction.*—Oersted's experiment, and the subsequent developments, had clearly shown how, at will, "to produce magnetism by electricity." Faraday seems to have held it as one of the tenets of his scientific philosophy that every physical relation (of cause and effect) has its converse. If electricity can produce magnetism, then magnetism should produce electricity. And in his notebook for 1822 appears the entry: "Convert magnetism into electricity." His repeated

[1] Quotation from Faraday's laboratory notebook, Sept. 3, 1821.

attempts failed. For example, in 1825, he tried what seemed to be the obvious converse by looking for an electric current in a helix of wire coiled around a magnet. Later, he tried to find a current in a wire placed near another wire carrying current. In 1828, is recorded another failure.

Faraday was not alone in his search for this converse effect. Fresnel, as early as November, 1820, had announced that he had succeeded in decomposing water by the current produced by a solenoid wound around a magnet. Later, he withdrew the statement. Ampère, likewise, made and subsequently withdrew a similar statement regarding the production of current from a magnet. Apparently, Ampère, later, became convinced that no such effect existed. They were all looking for the production of a *steady* current by placing a wire near a magnet.

But, several times, investigators were very near to the discovery of induced currents. In 1822, Ampère and de la Rive had observed a slight motion in a suspended copper coil when a magnet was approached. In 1824, Arago observed the damping of the vibrations of a magnetic needle suspended over a copper plate. This observation was extended by causing the needle to revolve by revolving the copper plate underneath it, air disturbances being, of course, eliminated. A little later, the converse effect (the causing of the copper disk to revolve by revolving the needle) was discovered. It was shown that this "dragging" effect was greater the greater the electrical conductivity of the spinning plate. Even the effect of radial slits in the copper disk, in reducing the dragging action on the magnet, was observed. But, suggestive as these experiments were, the real principle requisite to the "conversion of magnetism into electricity" remained undiscovered.

In the summer of 1831, Faraday attacked the problem for a fifth time. This time, instead of placing a *permanent* magnet inside a helix, he procured a soft iron ring 6 inches in external diameter, on which he wound two coils of copper, A and B, "separated by twine and calico." Coil A consisted of three lengths of wire each 24 feet long, "insulated from each other and capable of being connected as one length or used separately." Coil B consisted of two lengths of 30 feet each. To detect a possible current in coil B, he "connected its extremities by a copper wire passing to a distance and just over a magnetic needle." When coil A was connected to a battery, there was

"a sensible effect on the needle. It *oscillated* and settled at last in *original position*. On breaking connection of side *A* with battery, again a disturbance of the needle."

Slight as these momentary effects were, Faraday recognized their importance, although he had been looking for a *continuous* effect. On Aug. 30, he writes, "May not these transient effects be connected with causes of difference between power of metals at rest and in motion in Arago's experiments?"[1]

From this slender clue, Faraday proceeded rapidly to the discovery of the real effect. On the "third day" of his experiments, he wound a coil of wire around an iron cylinder and placed the cylinder so as to join the *N* pole of one permanent magnet with the *S* pole of another. The coil was connected to a galvanometer:

> Every time the magnetic contact at *N* or *S* was made or broken there was a magnetic action at the indicating helix [*i.e.*, galvanometer]—the effect being, as in former cases, not permanent but a mere momentary push or pull.

On the fourth day, he showed that the presence of iron was not necessary; that the effect was observed by the action of one helix on another.

The fifth day's experiment is best described in his own words:

> A cylindrical bar magnet . . . had one end just inserted into the end of the helix cylinder; then it was quickly thrust in the whole length and the galvanometer needle moved; then pulled out and again the needle moved, but in the opposite direction. The effect was repeated every time the magnet was put in or out, and therefore a wave of electricity was so produced from mere *approximation* of a magnet and not from its formation *in situ*.

At last! He had "converted magnetism into electricity." The essential requisite was *relative motion*, or a *change* of condition.

On the ninth day, he produced a continuous current by turning a copper disk between the poles of a powerful electromagnet, the periphery of the disk being connected to its axis through an indicating galvanometer. This was the now well-known Faraday disk dynamo, the *very first* dynamo-electric machine.

After only a few days' work in his laboratory, following, however, years of patient and persistent experiment, Faraday

[1] That is, the spinning copper disk mentioned above.

had discovered a phenomenon for which the greatest scientists of his time had sought in vain—electromagnetic induction, the importance of which to subsequent generations is almost beyond comprehension. It is to be doubted whether any single event in *all* history has had a greater effect on the *material* aspects of human society than has this discovery. For on it are founded modern electrical science and industry—indeed, almost the whole of our modern electrical age. Justly may Faraday be called the father of electrical science.

Following this discovery, Faraday devised and tried various electric machines to test and extend his newly discovered principle. One of these machines, consisting of a rotating rectangle of wire *with a commutator attached*, is, in every respect, the prototype of the modern dynamo. But his interest was always in pure science, for he writes:

> I have rather, however, been desirous of discovering new facts and relations dependent on magneto-electric induction, than of exalting the force of those already obtained; being assured that the latter would find their full development hereafter.

Being unacquainted with mathematical symbols and methods, Faraday always sought to explain his discoveries and to extend his researches by purely physical reasoning. To the mathematician, the law of magnetic attraction

$$F = \frac{m_1 m_2}{r^2}$$

may have been a sufficient explanation of the phenomenon, but to Faraday, this gave a statement only of the *magnitude* of the magnetic forces; *it left the phenomenon itself quite unexplained.* Accordingly, he insisted that two magnetic poles, or two electric charges, could act on each other *only if the medium between the two played some important part in the process.* This insistence on the importance of the medium ultimately led him to the very fruitful concept, at first qualitative but later quantitative, of lines of force and of the "*cutting*" of these lines as an essential process in electromagnetic induction. Three decades later, this concept became one of the corner stones of Maxwell's electromagnetic theory. Commenting on Faraday's laws of electromagnetic induction, Maxwell wrote:

> After nearly a half-century . . . , we may say that, though the practical applications of Faraday's discoveries have increased and are

increasing in number and value every year, no exception to the statement of these laws as given by Faraday has been discovered, no new law has been added to them, and Faraday's original statement remains to this day the only one which asserts no more than can be verified by experiment, and the only one by which the theory of the phenomena can be expressed in a manner which is exactly and numerically accurate, and at the same time within the range of elementary methods of exposition.

(*e*) *The Laws of Electrolysis.*—Faraday next turned his attention to proving that "Electricity, whatever may be its source[1] is identical in its nature." He found, for example, that electricity from a friction machine would deflect a galvanometer and would cause chemical decomposition just as would electricity produced by chemical action. And from his own experiments and those of others, he concluded that the different "kinds" of electricity differ not in character but only in degree.

This led him into the field of electrolysis. He first found that many substances, such as certain chlorides, nitrates, and sulphates, are non-conductors when solid but are good conductors when melted and that in the molten state they are decomposed by the passage of current. This showed that water was *not* essential to electrolysis. To clarify description of his experiments, he introduced the terms "electrode," "anode," "cathode," "ion," "anion," "cation," "electrolyte," "electrochemical equivalent," etc. A quantitative study of the whole phenomena resulted in his discovery of the laws of electrolysis which bear his name and which are the basis of all present-day work in that subject.

Further, Faraday clearly recognized that a definite quantity of electricity is associated with each atom or ion in electrolysis, and, had he been able to determine the number of atoms in unit mass of any substance, he would have anticipated, by 60 years, the determination of the fundamental charge *e*. For he says:

> Equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity; . . . it being the *electricity* which determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them.

(*f*) *The Conservation of Energy.*—In connection with a proof of the fact that the electricity from the voltaic pile results from

[1] That is, whether frictional, chemical, thermal, or electromagnetic.

chemical action and not from mere contact of one substance with another, Faraday stated clearly the doctrine of the conservation of energy several years before the statements of Mayer, Helmholtz, and Joule. In 1840, he wrote:

> The contact theory assumes that a force which is able to overcome a powerful resistance . . . can arise out of nothing . . . This would indeed be a creation of power, and is like no other force in nature. We have many processes by which the form of the power is so changed that an apparent conversion of one into the other takes place . . . But in no case is there a pure creation or a production of power *without a corresponding exhaustion of something to supply it.*

(*g*) *The "Faraday" Effect.*—Reference has already been made to Faraday's abhorrence of the doctrine of "action at a distance." He believed that, if two electric charges attract each other, the medium between the two takes part in the process. Presumably, therefore, the medium between two such charges is in a different state than it would be if the charges were not present, and if so, such an altered state should be detectable by observing the alteration in some physical property of the medium. As early as 1822, Faraday had experimented with a beam of polarized light passing through a transparent solution carrying a current, to see whether the current caused any "depolarizing" action. Although he repeated the experiment several times, in subsequent years, the results were all negative.

In 1845, he returned to the problem again, studying it very exhaustively, but with negative results. He then tried solid dielectrics with plates of metal foil connected to a powerful electric machine, to see whether, under electric strain, they would show any optical effects. No results![1]

Faraday then substituted a magnetic field for the electrostatic field, to see whether the former would cause any depolarizing action on the beam of light. Various substances were tried, but still with negative results. Finally, he placed in the magnetic field a very heavy piece of lead glass, which he had made many years earlier, and when the magnetic lines were parallel to the direction of the beam of polarized light, he observed that the plane of polarization was rotated. At last, he had found a relation between magnetism and light. This magnetic rotation is now known as the "Faraday effect." Again, his persistent

[1] Years later, this effect was found by Kerr.

search, maintained during 20 years of repeated failures, was rewarded by the discovery of an effect, of the existence of which he had the most sublime confidence.

(*h*) *Miscellaneous.*—Among Faraday's other researches may be mentioned: numerous investigations in chemistry; the liquefaction of several gases formerly thought "permanent"; the diffusion of gases through solids; self-induction; certain fundamental properties of dielectrics; diamagnetism; distinction between anode and cathode in the electric discharge through gases at low pressure; vibration of plates; regelation of ice; alloys of steel; and optical glass. If further proof be needed of the impress which Faraday left on physics, one need only recall the many times his name is used in physical terminology. Thus, we have the farad; the Faraday rotation (of a beam of polarized light); the Faraday dark space (in an electric discharge at low pressure); Faraday's Laws of Electrolysis; the Faraday cylinder; and the Faraday "ice pail" experiment.

Well may this simple, modest, self-taught philosopher be given a conspicuous place among the great benefactors of mankind.

5. Joseph Henry.—Any account of Faraday's work, however brief, should be accompanied by at least a mention of the researches of one of Faraday's illustrious contemporaries, the American physicist, Joseph Henry, whose memory is honored by the name of the unit of inductance, the henry, which bears to electrokinetics a relation identical with that of the farad to electrostatics.

Henry was born at Albany, New York, in 1799. Like Faraday, he became an apprentice at an early age, and, also like Faraday, his attention was called to science by the chance reading of a book on "Experimental Phylosophy." He entered the Albany Academy and, in 1826, became professor of mathematics. During the short summer vacations, only a single month, he experimented with such apparatus as he could make with his own hands. Independently of, but almost simultaneously with, Faraday, Henry discovered the laws of electromagnetic induction. But Faraday's results were published earlier than Henry's, and Faraday is justly credited with the discovery.

Henry devoted considerable attention to the improvement of electromagnets, invented by Sturgeon in England in 1825. Henry insulated the wire by silk thread; wound the wire in several layers instead of one; and introduced the "spool" con-

struction, which is standard today. He built one magnet which could support over four hundred times its own weight.

Extending these principles, Henry designed and constructed the first electric motor operating by an electromagnet. This was a sort of "push and pull" device consisting of an electromagnet, supported on pivots, so that it could rock back and forth between two permanent magnets, the current which energized the electromagnet being reversed at each "rock" by a suitable combination of mercury cups.

Henry's experiments on the operation of an electromagnet, located at a distance from the battery, led him to a clear understanding of the optimum conditions for securing maximum tractive effect. Thus, if the magnet were a long distance from the battery, both the cells of the battery and the "spools" of the electromagnet should be connected in series. While, if only short wires joined the magnet to the battery, the series connections should both be replaced by parallel connections. These discoveries led *directly* to the commercial development of the telegraph.

In the course of these experiments, Henry's attention was called to the intensity of the spark observed when a break is made in a circuit containing a long coiled wire through which a current is flowing. The effect was found to be intensified by coiling the wire into a close helix; but was diminished, or even absent, when the circuit consisted of only a short piece of uncoiled wire. Repeated trials with many modifications led him to the conclusion that the effect was due to the inductive action of the coil of wire upon itself. And in 1832, he announced the discovery of the phenomenon of self-induction in a paper[1] entitled "Electrical Self-induction in a Long Helical Wire."

In 1832, Henry was appointed to the chair of natural philosophy at Princeton. Here he continued his investigations on induced currents, and, in 1842, he was led to the important discovery that the discharge from a leyden jar is, under certain conditions, oscillatory. The importance of this discovery was not appreciated until over a decade later, when Lord Kelvin, as a result of a theoretical study, reached the conclusion that the discharge should be oscillatory.

The creative period of Henry's work in electricity ends with 1846, when he was appointed secretary of the Smithsonian Institution. Here, in spite of his official duties, he found time

[1] *Amer. Jour. Sci.*, vol. XXII, p. 408 (1832).

for an active interest in science. He organized a systematic method for the collection of meteorological data and for the making of daily weather maps. He contributed much to the improvement of lighthouses. And he was instrumental in organizing, under a federal charter, the National Academy of Sciences.

Henry died in 1878. When we consider his comparative isolation from the scientific atmosphere of Europe and his meager opportunities for carrying on research, we may well call him the "Dean of American Scientists."

6. James Clerk Maxwell.—It would be difficult to pick out two eminent scientists whose beginnings differed from each other more than did Maxwell's and Faraday's. Faraday came of very humble parentage; Maxwell, from a long line of distinguished ancestors. Faraday's early life was lived almost in poverty; Maxwell's family had abundant means. Faraday received only the most rudimentary education; Maxwell was given every advantage of school and university. They differed quite as much in their aptitude for scientific work. Faraday was one of the greatest exponents of experimental science which the world has ever seen; while Maxwell is one of the greatest figures in the entire history of theoretical physics. And yet both made indispensable and mutually supplementary contributions to the classical theories of electromagnetics.

Maxwell was born in Edinburgh in June, 1831, the very year when Faraday discovered electromagnetic induction. After an unsuccessful experience with a private tutor, young Maxwell, at the age of ten, was sent to the Edinburgh Academy.

> He was a friendly boy, though never quite amalgamating with the rest. But, however strange he sometimes seemed to his companions, he had three qualities which they could not fail to understand: agile strength of limb, imperturbable courage, and profound good nature.[1]

He was an all-around good student, but in geometry he made a particularly brilliant record. For, on Apr. 6, 1846, *two months before he was fifteen years old*, he presented a paper, by invitation, to the Royal Society of Edinburgh on "The Description of Oval Curves and Those Having a Plurality of Foci." At the same time, he was busy with experimental work on magnetism and polarized light. When he left the Academy, in 1847, he

[1] GLAZEBROOK: "James Clerk Maxwell and Modern Physics."

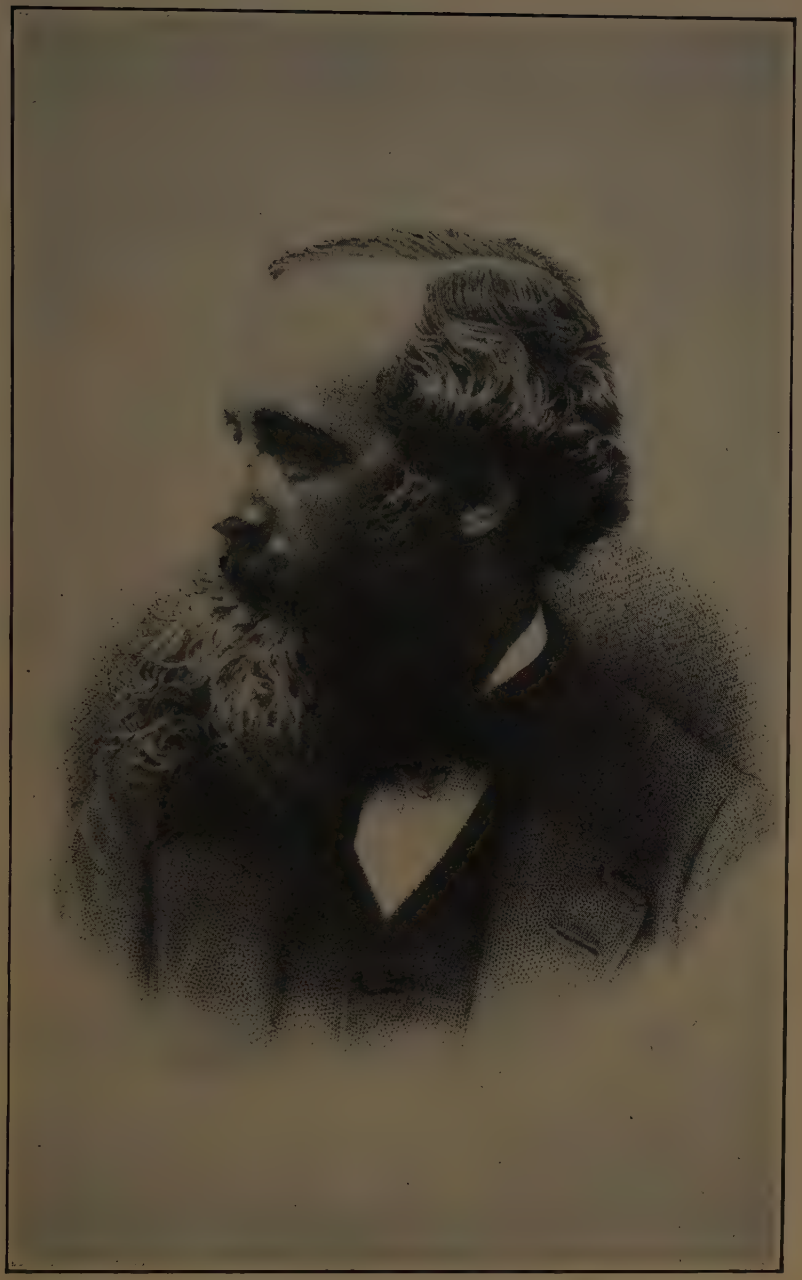

PLATE 6.—Maxwell.

(*Facing page* 72)

was "first in mathematics and in English and nearly first in Latin."

In November, 1847, Maxwell entered the University of Edinburgh, where, in addition to his studies in mathematics, natural philosophy, and logic, he prepared material for two important papers, the one on "The Theory of Rolling Curves," and the other on "The Equilibrium of Elastic Solids"—all this before he was nineteen years old!

But his interests were in experimental work as well as in theory. His description of his little laboratory on the family estate at Glenlair, where he spent his vacations, is interesting. In a letter to a friend, he writes:

> I have regularly set up shop now above the wash-house at the gate, in a garret. I have an old door set on two barrels, and two chairs, of which one is safe, . . .
>
> On the door there is a lot of bowls, jugs, plates, jam pigs, etc., containing water, salt, soda, sulphuric acid, blue vitriol, plumbago ore; also broken glass, iron, and copper wire, copper and zinc plate, bees' wax, sealing wax, clay, rosin, charcoal, a lens, a Smee's galvanic apparatus, and a countless variety of little beetles, spiders, and wood lice, which fall into the different liquids and poison themselves . . . I am experimenting on the best methods of electrotyping. So I am making copper seals with the device of a beetle. First, I thought a beetle was a good conductor, so I embedded one in wax (not at all cruel, because I slew him in boiling water in which he never kicked), leaving his back out; but he would not do. Then I took a cast of him in sealing wax, and pressed wax into the hollow, and blackleaded it with a brush; but neither would that do. So at last I took my fingers and rubbed it, which I find the best way to use the blacklead. Then it coppered famously.

A little later, he writes of experiments with jelly, under strain, exposed to polarized light; of "a notion for the torsion of wires and rods"; of plans for studying the relation between optical and mechanical constants, etc.

In 1850, Maxwell entered Trinity College, Cambridge, from which he graduated, in 1854, with high honors. After a short tenure as fellow at Trinity, he was appointed, in 1856, to the Professorship of Natural Philosophy at Aberdeen, a post which he held until 1860.

From 1860 to 1865, he was Professor at King's College, London. It was from here that some of his most important papers were

published, such as "Physical Lines of Force" (1862), and his greatest paper, "A Dynamical Theory of the Electromagnetic Field," read Dec. 8, 1864.

After a retirement of several years, Maxwell was, in 1870, elected to the newly founded Professorship of Experimental Physics at Cambridge. In this capacity, he superintended the planning and equipment of the now famous Cavendish Laboratory, of which he was director until his untimely death, on Nov. 5, 1879. A large proportion of Maxwell's papers, over one hundred in number, may be grouped under three headings: color vision; molecular theory; and electromagnetic theory.

The work on color vision was undertaken to make a quantitative study of the physical facts of the theory of color sensations proposed by Thomas Young, according to which any luminous sensation is the result of exciting, in the eye, three primary sensations, respectively, red, green, and violet. Young based his theory on his own experiments on spinning colored disks, by which he showed that any color may be matched by a mixture, in proper proportions, of these three primaries. Maxwell first verified this conclusion by experiments with his "color top." Then, to give his experiments greater definiteness, he invented a "color box," by means of which he could mix *spectral* colors, instead of colored papers. He expressed his measurements in a series of color equations, from which can be deduced the value of any color in terms of the three fundamental colors chosen as primaries. The results he expressed graphically both by the use of the "color triangle," previously employed by Young, and by plotting the three elementary sensations on a wave-length scale.

In the preface to "The Scientific Papers of James Clerk Maxwell," the editor, W. D. Niven, writes (1890):

> These observations, on which Maxwell expended great care and labour, constitute by far the most important data regarding the combinations of color sensations which have yet been obtained, and are of permanent value whatever theory may ultimately be adopted of the physiology of the perception of colour.

Maxwell, himself, clearly points out that his measurements are concerned with the *physics*, not the *physiology*, of color vision. For, at the conclusion of his paper, "Experiments on Colors as Perceived by the Eye,"[1] he writes:

[1] *Trans. Roy. Soc. Edinburgh*, vol. XXI.

The laws of sensation can be successfully investigated only after the corresponding physical laws have been ascertained, and the connection of these two kinds of laws can be apprehended only when the distinction between them is fully recognized.

Maxwell's work on molecular theory is so extensive as not to admit of brief abstract. He deduced, on rigorous mathematical grounds, the law of the distribution of velocities among the molecules of a gas. From consideration of coefficients of viscosity of gases, he determined the value of the "mean free path" and showed that the value thus obtained was in substantial agreement with the value which he computed from data on the diffusion of gases. He proved that

. . . the physical condition which determines that the temperature of two gases shall be the same, is that the mean kinetic energy of agitation of the individual molecules of the two gases are equal.

And he brought to bear upon the whole subject mathematical methods "in their generality and elegance, far in advance of anything previously attempted on the subject." Indeed, Maxwell is the co-founder with Clausius (1822–1888) of the kinetic theory of matter.

The electromagnetic theory is so intimately connected with modern physics as to warrant treatment in a separate chapter, in which, however, we shall not follow Maxwell's method. Maxwell states clearly that much of the experimental basis of his theoretical researches in electromagnetism was derived from Faraday's works. In the preface to the treatise, "Electricity and Magnetism," Maxwell writes:

Before I began the study of electricity I resolved to read no mathematics on the subject till I had first read through Faraday's "Experimental Researches on Electricity."

It is a noteworthy fact that in the early part of his speculations Maxwell made frequent use of analogies. In his first electrical paper on "Faraday's Lines of Force," published in 1856, he writes:

In order to obtain physical ideas without adopting a physical theory we must make ourselves familiar with the existence of physical analogies.

He then proceeds to develop the similarity between the electrical field and the steady flow of an incompressible fluid. In this

analogy, the mathematical expressions descriptive of one phenomenon are applicable to the other, provided "velocity of fluid" be correlated to "electrical force" and "difference of fluid pressure" to "difference of electrical potential."

In another connection, to get a mechanism to simulate the observed facts that "lines of force tend to contract longitudinally and to repel each other laterally," he likened a line of force to a string of spherical cells or sacks, with elastic walls and filled with an incompressible fluid, the whole string being in rotation about its axis. Each cell assumes the form of an oblate spheroid. Thus, the string tends to shorten longitudinally, and the equitorial bulge of each cell pushes neighboring strings laterally. If one end of such a string under tension be suddenly moved laterally, the disturbance will travel with finite velocity along the string.

By gradual steps, these analogies pointed out the real electromagnetic relations. And Maxwell clearly showed that all the facts of electrodynamics could be attributed to the action of a medium, the properties of which he deduced by rigorous mathematical reasoning. Maxwell's "Treatise on Electricity and Magnetism," published in 1873, which embodies these results, ranks with Newton's "Principia" as one of the most important books in all science.

The electromagnetic theory, as developed by Maxwell and extended by his successors, must be regarded as the crowning achievement of all but the last decade of the nineteenth century. And it is still, after more than 50 years, a large factor, perhaps even a dominating one, in present-day physics, whether one judges its greatness by the fertility of its application to the problems of pure science or by the more practical test of its value in the applied science of radio communication. For this reason, it is proper to discuss the elements of the electromagnetic theory as an integral part of the fascinating story of modern physics rather than as a part of the *history* of physics.

As previously mentioned, the third period in the history of physics ends about 1890, with the discovery of photoelectricity, the first of a group of phenomena the explanation of which require radical revision of some of the basic tenets of classical physics. Our discussion of the development of classical physics

from 1800 to 1890 has, of necessity, been confined to a few outstanding topics, such as: the mechanical theory of heat and the doctrine of the conservation of energy; the revival of the wave theory of light and, as we shall see in Chap. IV, its consolidation with the electromagnetic theory; the discovery of the phenomena of electromagnetism; and the development of the kinetic theory of matter. These fundamental principles seemed to cover so thoroughly and so adequately the entire field of physics that, as previously mentioned[1], a few scientists, some of them noted physicists, were inclined to the belief that all the *important* discoveries in physics had been made and that research henceforth would be concerned with studying details and with improving the technique of measurement "so as to investigate the next decimal place." How different our outlook in 1928!

The investigator in science is frequently likened to the explorer who penetrates the unknowns of the earth's surface. The similarity is striking, but there is this very important difference: Whereas the surface of the earth is finite, the extent of the unknowns in science may, so far as anything we now know, be infinite, at least in comparison with the present attainments of the human intellect. The Galileos, the Newtons, the Faradays, and the Maxwells will always find unsolved problems. Indeed, the progress of science is concerned, perhaps, not so much with solving problems as with finding problems to solve.

[1] Introduction, Sec. 8.

CHAPTER IV

THE ELECTROMAGNETIC THEORY OF LIGHT

It was pointed out, in Chap. III, that the wave theory of light, revived by Young in 1800, was put on a solid foundation by the discovery of the phenomena of interference and by the introduction of the concept of transverse vibrations to explain the phenomenon of polarization. This theory, as developed by Young, Arago, Fresnel, and their contemporaries, postulated an "ether" in which a light disturbance was propagated by transverse vibrations of a purely mechanical nature. The obvious difficulties more or less inherent in this "mechanical" ether in large part disappeared with the development of the electromagnetic theory of light by Maxwell who, while still retaining all the advantages of a transverse-wave theory, substituted for the mechanical vibrations of Young and Fresnel the vibrations of electric and magnetic vectors or, more simply, an *electromagnetic* vibration. It shall be the purpose of this chapter to develop the fundamental concepts of the electromagnetic theory of light to the point where the student may the more readily appreciate its conflict with the modern quantum theory, which will be discussed in subsequent chapters.

1. The Electrostatic System of Electrical Units.—Two electric charges whose magnitudes are designated by Q_1 and Q_2 act upon each other by a force f given by

$$f = \frac{1}{\epsilon} \frac{Q_1 Q_2}{r^2} \tag{1}$$

where ϵ is the dielectric constant of the medium between the charges and r is their distance apart. The quantity ϵ may be, for convenience, defined as the "ratio of the capacity of a parallel plate condenser with the medium concerned between its plates to the capacity of the same condenser when a vacuum is substituted for the dielectric." The electrostatic system defines *in the following order: quantity of electricity* (Q); *current* (i); (*electrostatic*) *field strength* (F).

(*a*) *The electrostatic unit of quantity* of electricity is a "point" charge[1] of such magnitude that if two such charges be placed 1 cm., *in vacuo*, from each other, the force of repulsion between the two will be 1 dyne. Similarly, if there is a mutual force action of Q dynes between an unknown point charge and a unit point charge when the two charges are 1 cm. apart, *in vacuo*, the unknown charge contains Q units of electricity. In equation (1), f is in dynes if Q_1 and Q_2 are measured in electrostatic units, as above defined, and r is given in centimeters. The customary definitions of positive and negative charges are assumed.

(*b*) *Current*, symbol i, in the electrostatic system is measured by the number of electrostatic units of quantity per second passing through a surface S. That is,

$$i = \frac{dQ}{dt} \tag{2}$$

where dQ is the quantity of electricity passing through S in time dt.

At any point, the current per square centimeter taken at right angles to the direction of flow is called the *current density*, symbol j, at that point. Both current and current density are *vector* quantities. The current density at a point may, therefore, be represented by a vector drawn from the point in the direction of current flow, the length of the vector being proportional to the *magnitude* of j. If, from the point in question as origin, a set of rectangular coordinate axes be drawn, then the projection of j on each of these axes may be taken as the *component* of j in the direction of that axis. If the axes be x, y, and z, the components of current density along these axes may be designated as j_x, j_y, and j_z, respectively.

The concept of current density and of the components of current density may be more readily grasped by considering the flow of current through a large rectangular mass of copper or through the electrolyte in a large rectangular tank. Imagine the current to enter at one corner and to leave at the opposite corner. Between these two points the current will follow the well-known "lines of flow." If the direction of flow at any point P be found, then the current density at that point is the current per square centimeter through a surface placed *at right angles* to the direction of flow. If one corner of the tank be taken as an

[1] That is, a charge placed upon a body whose dimensions are small compared to the distance to neighboring bodies or charges.

origin of coordinates x, y, and z, assumed parallel, respectively, to the three edges of the tank, then the current density at P in the x direction, *i.e.*, j_x, is measured by the current per square centimeter flowing through a surface containing P and placed parallel to the yz plane. And, similarly, one gets j_y and j_z.

(*c*) *The* (*electrostatic*) *field strength*, symbol F, at a point is defined as the "force in dynes acting on a unit electrostatic charge placed at the point." Since F is, thus, a vector quantity, we may resolve it into components along the x, y, and z axes, respectively. These components we shall call X, Y, and Z. Thus,

$$X = F \cos \theta_x$$

where θ_x is the angle between the direction of F and the x-axis. And so for Y and Z.

From the definition of field strength, it follows that the force f acting on a charge Q placed in a field of strength F is

$$f = F \cdot Q \tag{3}$$

2. The Electromagnetic System of Electrical Units.—Two magnetic poles whose magnitudes are designated by m_1 and m_2 act upon each other by a force f given by

$$f = \frac{1}{\mu} \frac{m_1 m_2}{r^2} \tag{4}$$

where μ is the permeability of the medium between the poles and r is their distance apart. The electromagnetic system defines, in the following order: magnetic pole (m); magnetic field (H); current (i'); quantity of electricity (Q').

(*a*) *The unit magnetic pole* is a "point" pole of such strength that if two such poles be placed 1 cm., *in vacuo*, from each other, the force of repulsion between the two will be 1 dyne. Similarly, if there is a mutual force action of m dynes between an unknown pole and a unit pole when the two poles are 1 cm. apart, *in vacuo*, the unknown pole is said to have a strength of "m units." In equation (4), f is given in dynes if m_1 and m_2 are measured in the above units, and r is in centimeters. The customary definitions of positive and negative poles are assumed.

(*b*) *The* (*magnetic*) *field strength*, symbol H, at a point is defined as the "force in dynes acting on a unit magnetic pole placed at the point." As in the case of the electrostatic field, we may resolve H into components along the x, y, and z axes, respectively. We shall call these components α, β, and γ.

(c) *The Electromagnetic Unit of Current.*—The definition of "current" in the electromagnetic system is based on the experimental fact that a wire carrying a current experiences a lateral force when placed in a magnetic field. *The electromagnetic unit of current* is defined as a "current of such strength that a wire, carrying the current and placed at right angles to a unit magnetic field, experiences a force of 1 dyne per centimeter in a direction perpendicular to both field and wire." The symbol for current, in these units, is taken as i'. (The ampere is one-tenth of this unit.)

Current density and *the components of current density* are defined in the electromagnetic system just as in the electrostatic system. As in the case of current, the electromagnetic quantities are distinguished from the corresponding electrostatic quantities by the prime ($'$). Thus, we have j', j'_x, j'_y, and j'_z for current density and the corresponding components.

The electromagnetic unit of *quantity of electricity* is defined as the "quantity of electricity carried per second through a surface through which 1 electromagnetic unit of current is flowing." We shall use the symbol Q' to designate quantity of electricity measured in these units. Since the order in which current and quantity are defined in the electromagnetic system is just the reverse of the corresponding order in the electrostatic system, it is logical to use the converse of equation (2) to determine quantity of electricity in the electromagnetic system; *i.e.*,

$$Q' = \int i'dt \qquad (5)$$

3. Ratio of the Two Systems of Units.—If we measure a given current first in electrostatic units and then in electromagnetic units, the numeric, i, in the former case, will be much larger than the numeric, i', in the latter, since the electrostatic unit is much smaller than the electromagnetic unit. The ratio i/i' of these two numerics is a very important physical quantity, which is customarily designated by the symbol c. Thus,

$$c = \frac{i}{i'} = \frac{\textit{number of electrostatic units in a given current}}{\textit{number of electromagnetic units in the same current}} \qquad (6)$$

In like manner,

$$c = \frac{Q}{Q'} \qquad (7)$$

This quantity c, therefore, is equal to the number of electrostatic units of current (or quantity) in 1 electromagnetic unit of current (or quantity).

Because of the fundamental importance of this ratio, it has been the subject of many researches by many different methods. Among the more important determinations may be mentioned the following:

Weber and Kohlrausch (1856)	$c = 3.107 \times 10^{10}$
Lord Kelvin (1869)	2.82
Rowland (1889)	2.98
Abraham (1890)	2.991
Rosa and Dorsey[1] (1907)	2.9971

4. Some Fundamental Formulae. (*a*) *La Place's Law.*—The magnetic field dH_P, at a point P, due to a short straight element ds of a circuit through which a (constant) current i' is flowing is given by

$$dH_P = \frac{i'ds}{r^2} \sin \theta \tag{8}$$

where ds is the length of the element; r is the distance from P to the element; and θ is the angle between the element and the line from the element to the point P. It should be remembered that dH is perpendicular to the plane including θ.

(*b*) *Field H Due to Current in a Long, Straight Wire.*—If a point P be a cm. distant from a very long,[2] straight wire carrying a current i', the magnetic field H_P at P is given by

$$H_P = \frac{2i'}{a} \tag{9}$$

This can be readily proven by integrating equation (8) over the entire length of the wire.

(*c*) *Work Done in Carrying a Unit Magnetic Pole Once around a Wire Carrying Current.*—A magnetic pole of strength m, placed a cm. from a long, straight wire, will experience a force f given, by use of equation (9), by:

$$f = mH_P = m \cdot \frac{2i'}{a} \tag{10}$$

[1] An excellent account of the various methods for measuring c and a detailed description of the method which they employed will be found in the article by ROSA and DORSEY, Bureau of Standards, *Bull.*, vol. 3, pp. 433, 541, and 605 (1907).

[2] That is, the length of the wire is very large compared to a.

If the pole be now carried around a circular path of radius a, concentric with the wire, an amount of work W will be done which is given by

$$W = m \cdot \frac{2i'}{a} \cdot 2\pi a$$
$$= 4\pi i' \cdot m \qquad (11)$$

Since equation (11) shows that W is independent of a, it is not necessary to restrict the motion of the pole to a circular path. If, therefore, a magnetic pole of strength m, starting at a point P, is caused to move along any path whatsoever which "links" once with a current i' (*i.e.*, if the pole ultimately returns to point P), the work done is given by equation (11). The work will be positive or negative according as the pole moves against, or in the direction of, the force.

5. Maxwell's Differential Equations of the Electromagnetic Field.—(*a*) Consider a point O *inside* a conductor through which a current is flowing. It may help the student to visualize the arrangement if the conductor be thought of as the large tank of electrolytic solution with current entering at one point and leaving at another point, O being somewhere within the tank. With point O as origin, construct a set of rectangular axes Ox, Oy, and Oz (Fig. 1), so oriented, for simplicity, that the current in the neighborhood of O flows parallel to the z-axis, say in the direction zO. Let the *density* of this current be j_z', assumed constant in the immediate neighborhood of O.

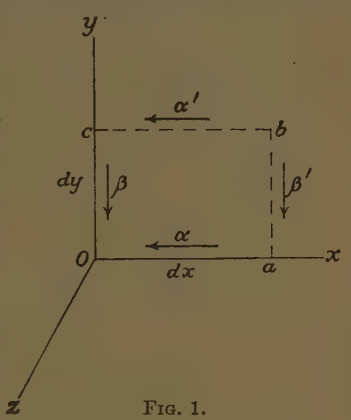

FIG. 1.

Consider a small elementary rectangle $Oabc$ in the x-y plane, the length of whose sides are dx and dy, and whose area, therefore, is $dx \cdot dy$. The current di_z' flowing through (*i.e.*, in this case, at right angles to) this rectangle is given by

$$di_z' = j_z' dx dy \qquad (12)$$

Further, assume that in the neighborhood of O there is produced by the currents and, possibly, by external magnetic poles a magnetic field whose components α, α', β, β' along the respective

sides of the rectangle are as shown in the figure. In general, α' will differ from α, and β' from β.

If, now, a unit magnetic pole, starting from O, be carried, say counterclockwise, once around the rectangle, the path of the pole will "link" once with the current di_z' flowing through the rectangle. The work dW done during this process may be computed in either of two ways: (a), by equations (11) and (12)

$$\begin{aligned} dW &= 4\pi di_z' \\ &= 4\pi j_z' \cdot dxdy; \end{aligned} \tag{13}$$

or (b) we may compute the work done in carrying the pole along each of the four rectilinear paths Oa, ab, bc, and cO and then add. Thus,

$$dW = \alpha \cdot dx + \beta' \cdot dy - \alpha' \cdot dx - \beta \cdot dy \tag{14}$$

We can simplify equation (14). Let the curve def, in Fig. 2, show the variation of β with x in the neighborhood of point O, β and β' of Fig. 2 being identically the same as β and β' of Fig. 1, and dx of Fig. 2 being the same as dx of Fig. 1. If the slope of this curve in the neighborhood of e be $\partial\beta/\partial x$, it at once follows that

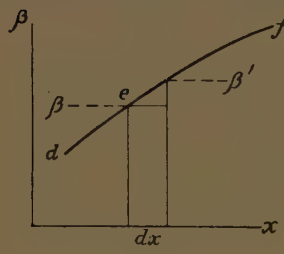

FIG. 2.

$$\beta' = \beta + \frac{\partial \beta}{\partial x} dx \tag{15}$$

and, similarly,

$$\alpha' = \alpha + \frac{\partial \alpha}{\partial y} dy \tag{16}$$

If the values of α' and of β' from equations (15) and (16) be put in equation (14), there results

$$\begin{aligned} dW &= \alpha \cdot dx + \left(\beta + \frac{\partial \beta}{\partial x} dx\right) dy - \left(\alpha + \frac{\partial \alpha}{\partial y} dy\right) dx - \beta \cdot dy \\ &= \left(\frac{\partial \beta}{\partial x} - \frac{\partial \alpha}{\partial y}\right) dx\, dy \end{aligned} \tag{17}$$

It is obvious that equations (13) and (17) must give identical values of dW. We may, therefore, write,

$$\begin{aligned} 4\pi j_z' \cdot dxdy &= \left(\frac{\partial \beta}{\partial x} - \frac{\partial \alpha}{\partial y}\right) dxdy \\ \therefore 4\pi j_z' &= \frac{\partial \beta}{\partial x} - \frac{\partial \alpha}{\partial y} \end{aligned} \tag{18}$$

In this equation, current is measured in electromagnetic units. We may introduce current measured in electrostatic units by using equation (6) according to which $j_z' = j_z/c$. We may, then, write,

$$\frac{4\pi}{c} j_z = \frac{\partial \beta}{\partial x} - \frac{\partial \alpha}{\partial y} \tag{19}$$

(*b*) In setting up Fig. 1, we arbitrarily oriented the system of axes so that Oz was parallel to the direction of current at O. For this orientation, j_x' and j_y' are each zero. This limitation is obviously unnecessary. If the coordinate axes have any arbitrary direction with respect to the current, j_x' and j_y' will not, in general, be zero, and we shall have for each of them an equation similar to equation (19). We might derive each of these equations in the same way as equation (19) was derived. But it is more instructive to consider the symmetrical relations existing among the several quantities.

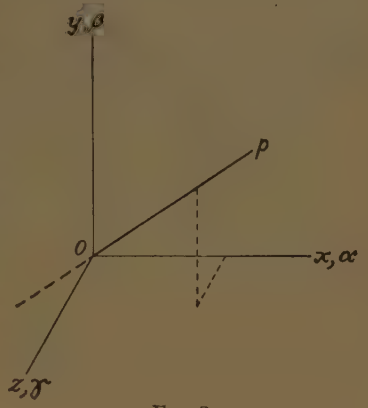

FIG. 3.

Let Fig. 3 represent the coordinate axes x, y, z, with which are associated, respectively, the components α, β, γ, of a magnetic field. Let Op be a line drawn so as to make equal angles with the three axes. Equation (19) shows a relation between j_z and quantities belonging to the xy plane. An exactly similar relation must exist between j_x and quantities belong to the yz plane. To find this relation, imagine the whole figure rotated clockwise 120 degrees about Op as an axis, so that the new position of the y-axis coincides with the previous position of the x-axis. The direction of j_z will then coincide with the previous direction of j_z, and we may represent the transitions by

$$\begin{array}{lll} y \rightarrow x & \beta \rightarrow \alpha & j_y \rightarrow j_x \\ x \rightarrow z & \alpha \rightarrow \gamma & j_x \rightarrow j_z \\ z \rightarrow y & \gamma \rightarrow \beta & j_z \rightarrow j_y \end{array} \tag{20}$$

where the symbol $\rightarrow$ means "takes the place of." We may represent these cyclical relations by Fig. 4. Having derived one equation, such as equation (19), the other two equations may be

written by means of the "replacements" indicated in Fig. 4. Thus, we have

$$\frac{4\pi}{c} j_x = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} \tag{21a}$$

$$\frac{4\pi}{c} j_y = \frac{\partial \alpha}{\partial z} - \frac{\partial \gamma}{\partial x} \tag{21b}$$

$$\frac{4\pi}{c} j_z = \frac{\partial \beta}{\partial x} - \frac{\partial \alpha}{\partial y} \tag{21c}$$

Equations (21) are in entire harmony, as, of course, they should be, with our elementary concepts. The left-hand members contain currents. The right-hand members contain *space* rates of variation of magnetic fields. For example, if a current flows, let us say, along a very long wire, in the x direction,

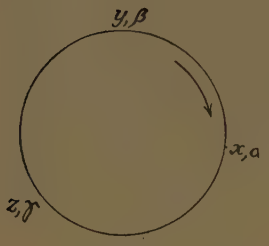

FIG. 4.

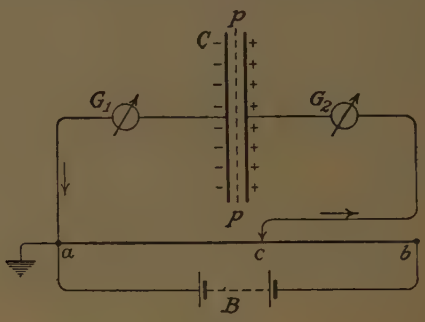

FIG. 5.

the resulting magnetic field around the wire is independent of x, but it *does* depend on y and z. This is in accord with equation (21a). Further, the left-hand side of equation (21a) represents the work which would be done in carrying a unit magnetic pole once around an area 1 cm. square through which a current j_x is flowing. If $\partial y = \partial z = 1$ cm., the right-hand side of equation (21a) is easily seen to give exactly the same quantity of work.

(*c*) *Displacement Currents.*—Maxwell regarded electricity as behaving like an incompressible fluid. Consider the circuit shown in Fig. 5. A battery B is connected to a long resistance ab on which is a sliding contact c. Points a and c are connected through galvanometers G_1 and G_2 to the plates of a condenser C. (Assume, for the moment, that there is a vacuum between the plates.) If c, starting from coincidence with a, moves *uniformly* toward b so as to increase uniformly the potential difference

between the plates of the condenser, thereby increasing its charge, a *constant* current, say i, will flow through the galvanometer G_1, and an identical current through G_2. Except for the condenser, the circuit aG_1G_2c might be regarded as a *continuous* circuit. No current *actually* flows between the plates of the condenser; but during the charging process, the electric field between the plates is *increasing at a uniform rate. We may regard the phenomena which happen in the space between the plates to be exactly the same as if a constant current* i, the displacement current of Maxwell, *were really flowing between the plates.* We can correlate this rate of increase of electric field with the equivalent (or displacement) current i, as follows:

Let the area of either plate of the condenser be A. (Assume the distance between the plates very small compared to their lateral dimensions.) Then, when, at any instant, there is a charge Q on the plates, the number of lines of force per square centimeter between the plates, which number is numerically equal to the field strength F between the plates, is given by

$$F = 4\pi\frac{Q}{A} \tag{22}$$

The simultaneous rates of change of F and Q are given by

$$\frac{dF}{dt} = 4\pi \cdot \frac{1}{A} \cdot \frac{dQ}{dt} \tag{23}$$

But

$$\frac{dQ}{dt} = i$$

and

$$\frac{1}{A}\frac{dQ}{dt} = j$$

where j is the *equivalent* current density through the surface. We may therefore write equation (23) as

$$\frac{dF}{dt} = 4\pi j \tag{24}$$

$$\therefore j = \frac{1}{4\pi} \cdot \frac{dF}{dt} \tag{25}$$

That is to say, if, at any point in (empty) space, the electric field F is changing at a rate dF/dt, we may regard the phenomena resulting therefrom as identical with what would happen *if* a current of density j given by equation (25) were actually flowing through the same region in the direction of the *change* of F.

If, instead of a vacuum, there is between the plates of the condenser a medium whose dielectric constant is ϵ, equation (22) should be written

$$F = \frac{4\pi}{\epsilon} \cdot \frac{Q}{A} \tag{26}$$

and equation (25) would, then, become

$$j = \frac{\epsilon}{4\pi} \cdot \frac{dF}{dt} \tag{27}$$

An alternative method of deriving equation (25) lays greater emphasis on the concept of electricity as behaving like an incompressible fluid. Consider, first, an analogy. Imagine a large vessel, filled with an incompressible fluid, say water, into the side of which projects a tube t, (Fig. 6). Over the inside end of t

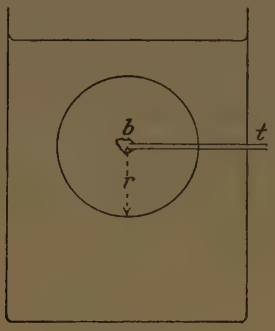

FIG. 6.

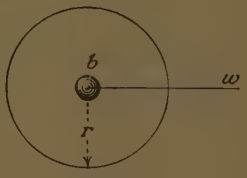

FIG. 7.

is fitted a completely deflated toy balloon b. Describe around b an imaginary sphere of radius r. Now, let a volume of water V be inserted into b through t. The balloon will be inflated and will occupy a volume V. An equal volume of water will be *displaced* outward through the surface of the imaginary sphere. And it is readily seen that the average displacement through unit area of the sphere is $V/(4\pi r^2)$.

The electrical analogue is obvious. Suppose that an insulated metal ball (b, Fig. 7) is being charged at a uniform rate by means of the wire w. We describe the phenomenon by saying that the charge remains on the ball and that there is produced an electric field in the neighborhood. But we might consider that the electricity behaves as does the water in the analogy and that, if

the ball has received a charge Q, a quantity of electricity equal to Q has been *displaced* outward through the surface of an imaginary sphere of radius r concentric with b. This *imaginary* displacement of electricity is *equivalent to* the *actual* change of electric field. For, consider the ball to be surrounded by a medium whose dielectric constant is ϵ. Then, if, at a given instant, the charge on the ball is Q, the electric field F at the surface of the sphere will be (neglecting the dissymmetry introduced by the wire)

$$F = \frac{1}{\epsilon}\frac{Q}{r^2} \tag{28}$$

and the rate of increase of F as Q increases will be

$$\begin{aligned}\frac{dF}{dt} &= \frac{1}{\epsilon}\cdot\frac{1}{r^2}\cdot\frac{dQ}{dt} \\ &= \frac{4\pi}{\epsilon}\cdot\frac{1}{4\pi r^2}\cdot\frac{dQ}{dt}\end{aligned} \tag{29}$$

But $4\pi r^2$ is the area of the imaginary sphere; and dQ/dt, the current flowing *onto* the ball, is also the *equivalent* (*i.e.*, displacement) current flowing outward through the entire surface of the sphere. The equivalent current per unit area through the sphere, *i.e.*, the current density j, is, therefore, given by

$$j = \frac{1}{4\pi r^2}\cdot\frac{dQ}{dt}$$

Accordingly, we may write equation (29) in the form

$$\frac{dF}{dt} = \frac{4\pi}{\epsilon}\cdot j$$

or, as before (equation (27)),

$$j = \frac{\epsilon}{4\pi}\cdot\frac{dF}{dt} \tag{27}$$

It should be emphasized that the direction of this equivalent current density j is the same as the direction of the *rate of change* of F. In the foregoing discussion, we have considered the change of F to be due to a change in the *magnitude* of the charge producing F. But the field F at a given point, due to a charge Q, may be changed by changing the *position* of the charge. Thus, consider a charge $+Q$ (Fig. 8) moving toward the right with a velocity

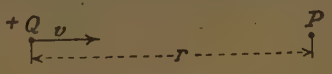

FIG. 8.

v. The electric field at P will increase. Assuming the system to be in a vacuum, the electric field F_P at P is given by

$$F_P = \frac{Q}{r^2}.$$

at the instant when Q is distant r from P. At that instant, the rate of change of F_P is given by

$$\frac{dF_P}{dt} = -2\frac{Q}{r^3}\cdot\frac{dr}{dt}$$

$$\because \frac{dr}{dt} = v$$

$$\therefore \frac{dF_P}{dt} = -2\frac{Qv}{r^3}$$

and, from equation (27), the equivalent current density j_P at P is given by

$$j_P = -\frac{\epsilon}{4\pi}\cdot\frac{2Qv}{r^3} \tag{30}$$

In the case just considered, the *direction* of F remains constant. But we may have a change of F occasioned by a change in its

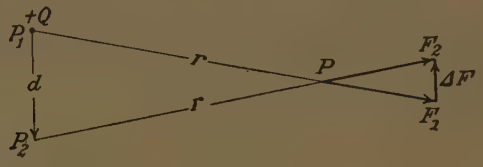

FIG. 9.

direction without change of magnitude. In Fig. 9, let the charge $+Q$ pass at a uniform velocity v from point P_1 to P_2. When Q is at P_1, the field F_1 at P is

$$F_1 = \frac{Q}{r^2}$$

When Q reaches P_2, the field F_2 at P has the same numerical value but has changed in direction, and there has been a change ΔF in F, as shown. If Δt has been the time required for Q to pass from P_1 to P_2, the average rate of change of F is given by

$$\frac{\Delta F}{\Delta t}$$

It is left to the reader to compute the current density of the displacement current equivalent to this change in F. (For simplicity, take the case where r is large compared to d.)

In general, neither F nor its rate of change will be directed along one of the coordinate axes x, y, z. And just as F has components X, Y, Z so dF/dt has corresponding components

$$\frac{\partial X}{\partial t}, \frac{\partial Y}{\partial t}, \frac{\partial Z}{\partial t}$$

(*d*) We may now regard equations (21), which were developed by considering the case of an actual current of density j, to apply to the case where, instead of the actual current, we have a so-called "displacement current" resulting from a (time) rate of change of electric field, provided we make the substitutions for the components of current density, in accordance with equation (27), *viz.*,

$$j_x = \frac{\epsilon}{4\pi}\frac{\partial X}{\partial t}$$

$$j_y = \frac{\epsilon}{4\pi}\frac{\partial Y}{\partial t}$$

$$j_z = \frac{\epsilon}{4\pi}\frac{\partial Z}{\partial t}$$

We then have

$$\frac{\epsilon}{c}\frac{\partial X}{\partial t} = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} \qquad (31a)$$

$$\frac{\epsilon}{c}\frac{\partial Y}{\partial t} = \frac{\partial \alpha}{\partial z} - \frac{\partial \gamma}{\partial x} \qquad (31b)$$

$$\frac{\epsilon}{c}\frac{\partial Z}{\partial t} = \frac{\partial \beta}{\partial x} - \frac{\partial \alpha}{\partial y} \qquad (31c)$$

(*e*) These equations (31) are the first set of Maxwell's equations of the electromagnetic field. It is to be noted that they express the *time* rates of change of electric fields (left-hand members) in terms of the *space* rates of change of magnetic fields.

These equations contain no essentially new physical principles; they simply put in rigorous mathematical form some very elementary concepts. For, consider, again, a long, straight wire w_1w_2 through which a *constant* current is flowing. Such a wire is surrounded by a magnetic field. We *say* that the *current* produces the field. But let us examine the phenomenon a little more closely. We regard the current, nowadays, as made up of a succession of moving charges, *i.e.*, electrons—really, negative charges. A negative charge moving toward the left is equivalent to a positive charge moving toward the right. Let us repre-

sent the current through the wire as a procession of positive charges (Fig. 10) moving at uniform speed toward the right, say in the positive direction of x. The magnetic field produced by such a wire carrying a current is, as we know from experiment, represented by a series of concentric circles, drawn about the wire as a center and in planes at right angles to the wire. The direction of these circular fields is clockwise looking in the positive x direction. One of these circles is represented as drawn about point a on the wire. *The magnetic field at some point, such as P_1, must, in reality, be the sum total of the effects at P_1 due to the motion of each of the individual charges.* In other words, each of the moving charges, say e_1, produces a magnetic field at P_1 irrespective of the motion or presence in the wire of any other charge such as e_2. That is, even if e_1 were *alone* and were moving

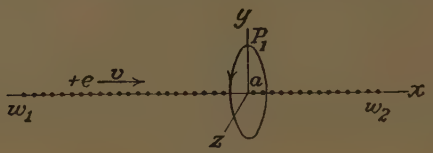

FIG. 10.

in the direction indicated, it would produce a magnetic field at P_1. Now, the only means, so far as we know, by which a charge can produce *any* effect at some outside point is through the agency of the *electric* field which surrounds the charge. So long as the charge e_1 is stationary, although there is an electric field produced at P_1, there is no magnetic field. When, however, e_1 is moving toward a, the electric field at P_1 due to e_1 changes, and we *observe* that, simultaneously, there is produced at P_1 a magnetic field. Viewed from this standpoint, therefore, we may regard the production of the magnetic field around a wire carrying current as due, in reality, to the change (with time) of the electric fields due to the moving charges. Or, to generalize, a changing electric field produces a magnetic field—which is exactly what equations (31) tell us. Further, a glance at Fig. 10 shows that the direction of the magnetic field at P_1 is at right angles to the direction of the rate of change of electric field at that point due to the motion of e_1. This fact is, also, contained in equations (31).

(*f*) *The Second Set of Electromagnetic Equations.*—Experiment shows us that there are mutually reciprocal relations between electric and magnetic fields. According to the previous para-

graph, a moving positive charge Q will produce magnetic fields which are related to its direction of motion, as shown in Fig. 11(a). On the other hand (Fig. 11(b)), a positive magnetic pole m, moving toward the right, will generate a counterclockwise current in a circular loop of wire placed at a. Of course, the electric field F, produced by the motion of the pole, will exist, whether the loop of wire be present or not. That is to say, a changing magnetic field produces an electric field which is constant if the *rate of change* of magnetic field is constant. This is, of course, the law of induced electromotive forces discovered by Faraday.

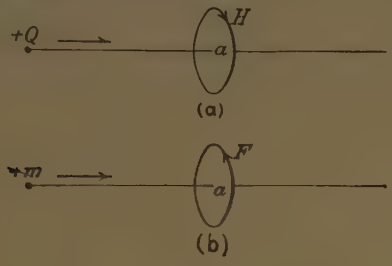

FIG. 11.

The phenomena represented in Fig. 11(a) are expressed mathematically in equations (31). The phenomena represented in Fig. 11(b) may be represented by an exactly analogous set of equations which express time rates of change of *magnetic fields* (left-hand members) in terms of space rates of change of *electrostatic fields* (right-hand members) by making the three following changes in equations (31)

1. Replace the components of electric field X, Y, Z in the left-hand members by the corresponding components of magnetic field α, β, γ; and *vice versa* in the right-hand members.
2. Replace the dielectric constant ϵ by the permeability μ, since it is seen from equation (1) and (4) that these two quantities play analogous roles in the respective phenomena.
3. Change the signs of each term of the right-hand members, since, by comparing Figs. 11(a) and (b), it is seen that the direction of the magnetic field in Fig. 11(a) (clockwise) is opposite to the direction of the electric field in Fig. 11(b) (counterclockwise).

There then results the second set of electromagnetic equations, *viz.*,

$$\frac{\mu}{c} \cdot \frac{\partial \alpha}{\partial t} = -\left(\frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z}\right) \tag{32a}$$

$$\frac{\mu}{c} \cdot \frac{\partial \beta}{\partial t} = -\left(\frac{\partial X}{\partial z} - \frac{\partial Z}{\partial x}\right) \tag{32b}$$

$$\frac{\mu}{c} \cdot \frac{\partial \gamma}{\partial t} = -\left(\frac{\partial Y}{\partial x} - \frac{\partial X}{\partial y}\right) \tag{32c}$$

Equations (32) might have been derived quite independent of equations (31) by a method exactly analogous to the method used for the derivation of equations (31).[1]

6. The Differential Equations of the Electromagnetic Wave.—(*a*) We may combine equations (31) and (32), as follows:

1. Differentiate both sides of equation (31*a*) with respect to t:

$$\frac{\epsilon}{c} \cdot \frac{\partial^2 X}{\partial t^2} = \frac{\partial^2 \gamma}{\partial y \partial t} - \frac{\partial^2 \beta}{\partial z \partial t} \tag{33}$$

2. Differentiate equation (32*b*) with respect to z:

$$\frac{\mu}{c} \cdot \frac{\partial^2 \beta}{\partial z \partial t} = -\frac{\partial^2 X}{\partial z^2} + \frac{\partial^2 Z}{\partial x \partial z} \tag{34}$$

3. Differentiate equation (32*c*) with respect to y:

$$\frac{\mu}{c} \cdot \frac{\partial^2 \gamma}{\partial y \partial t} = -\frac{\partial^2 Y}{\partial x \partial y} + \frac{\partial^2 X}{\partial y^2} \tag{35}$$

4. Replace each of the two right-hand terms of equation (33) by their equivalents, as determined from equations (34) and (35):

$$\frac{\epsilon}{c} \cdot \frac{\partial^2 X}{\partial t^2} = \frac{c}{\mu}\left(\frac{\partial^2 X}{\partial y^2} - \frac{\partial^2 Y}{\partial x \partial y} - \frac{\partial^2 Z}{\partial x \partial z} + \frac{\partial^2 X}{\partial z^2}\right) \tag{36}$$

5. By adding and subtracting $\partial^2 X/\partial x^2$ within the bracket on the right-hand side of equation (36), we have, after rearranging,

$$\frac{\mu\epsilon}{c^2} \cdot \frac{\partial^2 X}{\partial t^2} = \left(\frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} + \frac{\partial^2 X}{\partial z^2}\right) - \left(\frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 Y}{\partial x \partial y} + \frac{\partial^2 Z}{\partial x \partial z}\right) \tag{37}$$

Magnetic fields no longer appear in equation (37). Instead, we have second derivatives of electrostatic fields.

[1] DRUDE: "Theory of Optics," translated by Mann and Millikan, p. 265.

(*b*) Let us now discuss the second bracket on the right-hand side of equation (37). Since each term of this bracket is differentiated with respect to x, we may write it as follows:

$$\frac{\partial}{\partial x}\left(\frac{\partial X}{\partial x}+\frac{\partial Y}{\partial y}+\frac{\partial Z}{\partial z}\right) \tag{38}$$

Consider a small, rectangular parallelepiped (Fig. 12), whose sides are, respectively, dx, dy, dz, placed in *any* given location with respect to a coordinate system x, y, z. Assume that there are, in the neighborhood, electric fields due to any distribution of charges, and, to make the problem concrete, assume that the resultant field, near the parallelepiped, is directed in the general direction away from the origin. Lines of force will then *enter* the parallelepiped through the left, the front, and the bottom faces and will *leave* through the right, the rear, and the top faces. *If there are no free charges within the parallelepiped*, as many lines must enter it as leave. Or, calling lines which enter "positive" and lines which leave "negative," we may say that the sum of lines entering plus those leaving is zero. We may express this fact in the following way:

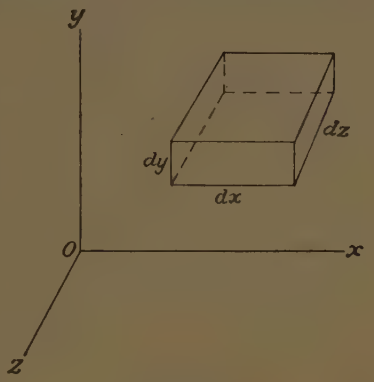

FIG. 12.

Let X and X' be the (average) intensities of the x components of the electric field over the left- and the right-hand faces, respectively. Then $X dydz$ lines enter the left-hand face and $X' dydz$ lines leave the right-hand face. Letting Y, Y' and Z, Z' refer, similarly, to the other four faces, we may write:

$$(X - X')dydz + (Y - Y')dxdz + (Z - Z')dxdy = 0 \tag{39}$$

By a method exactly analogous to that used in deriving equations (15) and (16), we obtain relations between X and X', Y and Y', Z and Z', as follows:

$$\begin{aligned} X' &= X + \frac{\partial X}{\partial x}dx \\ Y' &= Y + \frac{\partial Y}{\partial y}dy \\ Z' &= Z + \frac{\partial Z}{\partial z}dz \end{aligned} \tag{40}$$

Putting these values of X', Y', Z' from equations (40) in equation (39), we have, after canceling the identical terms having opposite signs,

$$\left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} + \frac{\partial Z}{\partial z}\right) dxdydz = 0 \tag{41}$$

But $dx \cdot dy \cdot dz$ is the volume of the parallelopiped. Since this volume is not zero, it follows that the parenthesis of equation (41) must be zero. *i.e.*,

$$\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} + \frac{\partial Z}{\partial z} = 0 \tag{42}$$

Now, the parallelopiped was arbitrarily located. Hence equation (42) is true *for all locations*, or for all values of the coordinates. Therefore, the quantity (38) is equal to zero; *i.e.*,

$$\frac{\partial}{\partial x}\left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} + \frac{\partial Z}{\partial z}\right) = 0 \tag{43}$$

In passing, attention should be called to the fact that, in setting up equation (39), we assumed that there were no free charges within the parallelepiped. If, however, we assume that there are free (positive, say) charges within the parallelepiped to the extent of ρ per unit volume, or $\rho \cdot dx \cdot dy \cdot dz$ within the whole volume, the number of lines which leave will be in excess of those which enter by $4\pi\rho dxdydz$. We should, then, write, instead of equation (34),

$$(X - X')dydz + (Y - Y')dxdz + (Z - Z')dxdy = -4\pi\rho dxdydz \tag{44}$$

Equation (42) then becomes

$$\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} + \frac{\partial Z}{\partial z} = -4\pi\rho \tag{45}$$

In vector notation, the left-hand side of equation (45), or of equation (42), is spoken of as the *divergence* (*div*) of the electric vector F. And equations (42) and (45) may be written, respectively,

$$div\ F = 0 \tag{42'}$$

$$div\ F = -4\pi\rho \tag{45'}$$

(*c*) Equation (43) shows that, if we consider a region in which there are no free charges, the second term on the right side of equation (37) is zero. And we may write,

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 X}{\partial t^2} = \frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} + \frac{\partial^2 X}{\partial z^2} \tag{46}$$

This equation (46) was derived by the series of steps given on page 94. It is obvious that, if we start by differentiating the equation (31*b*) with respect to time and equations (32*a*) and (32*c*) with respect to z and x, respectively, we should obtain for the component Y an equation similar to equation (46). Proceeding in this way, one may obtain equations for each of the components of the electric and the magnetic fields. These six equations are as follows:

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 X}{\partial t^2} = \frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} + \frac{\partial^2 X}{\partial z^2} \qquad (47a)$$

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 Y}{\partial t^2} = \frac{\partial^2 Y}{\partial x^2} + \frac{\partial^2 Y}{\partial y^2} + \frac{\partial^2 Y}{\partial z^2} \qquad (47b)$$

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 Z}{\partial t^2} = \frac{\partial^2 Z}{\partial x^2} + \frac{\partial^2 Z}{\partial y^2} + \frac{\partial^2 Z}{\partial z^2} \qquad (47c)$$

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 \alpha}{\partial t^2} = \frac{\partial^2 \alpha}{\partial x^2} + \frac{\partial^2 \alpha}{\partial y^2} + \frac{\partial^2 \alpha}{\partial z^2} \qquad (48a)$$

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 \beta}{\partial t^2} = \frac{\partial^2 \beta}{\partial x^2} + \frac{\partial^2 \beta}{\partial y^2} + \frac{\partial^2 \beta}{\partial z^2} \qquad (48b)$$

$$\frac{\mu\epsilon}{c^2}\frac{\partial^2 \gamma}{\partial t^2} = \frac{\partial^2 \gamma}{\partial x^2} + \frac{\partial^2 \gamma}{\partial y^2} + \frac{\partial^2 \gamma}{\partial z^2} \qquad (48c)$$

(*d*) *General Equations of Wave Motion.*—It now remains to interpret these equations (47) and (48). They can be shown to represent the differential equations of a wave motion. Consider, first, a simple case of a wave motion along a string.

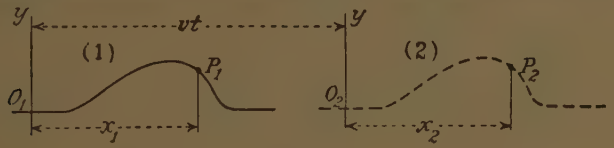

FIG. 13.

In Fig. 13, let a string be stretched initially so as to coincide with the x-axis. Let the string be then given (say by a transverse blow) a "disturbance," such as is shown at (*1*), and let this disturbance travel, as a wave, toward the right, with a velocity v. The magnitude of v will depend on the tension and the mass per unit length of the string. The "wave form," that is to say, the displacements in the y direction of the several parts of the string, is, of course, some function, say the f function, of x. If we measure x and y from O_1, we may write

$$y = f(x_1) \qquad (49)$$

After a time, t, the disturbance will have reached position (*2*). If we imagine the origin to have been carried along with the wave, the new position of the origin will be at O_2, a distance $v \cdot t$ from O_1. If we assume that the string is homogeneous and that there is no damping, it can be shown that the *form* of the wave at (*2*) will be *exactly* the same as the form at (*1*). That is, measuring x from O_2, the displacement of the string at (*2*) will be *exactly* the same function of x_2 as it previously was of x_1 at position (*1*). And we may write, for position (*2*)

$$y = f(x_2) \tag{50}$$

If, however, we wish to continue to measure x from O_1, we must replace x_2 in equation (50) by

$$x_2 = x_1 - vt \tag{51}$$

where x_1 now refers to distance O_1P_2 and to time t. Hence, we may write equation (50):

$$y = f(x_1 - vt) \tag{52}$$

This equation represents the wave motion under consideration. It is to be noted that y is here a *displacement*.

We now proceed to derive the *differential* equation of this wave motion. Differentiate equation (52) with respect to t and x,[1] respectively:

$$\frac{\partial y}{\partial t} = -vf'(x - vt) \tag{53a}$$

$$\frac{\partial y}{\partial x} = f'(x - vt) \tag{53b}$$

$$\therefore \frac{\partial y}{\partial t} = -v\frac{\partial y}{\partial x} \tag{54}$$

Differentiating again gives

$$\frac{\partial^2 y}{\partial t^2} = v^2 f''(x - vt) \tag{55a}$$

$$\frac{\partial^2 y}{\partial x^2} = f''(x - vt) \tag{55b}$$

$$\therefore \frac{\partial^2 y}{\partial t^2} = v^2\frac{\partial^2 y}{\partial x^2} \tag{56}$$

(The functions f' and f'' are, of course, the first and second derivatives of the function f.)

Equation (56) is the differential equation sought. It represents a plane-polarized (transverse) wave traveling along the x-axis and is seen to be independent of the function f of equation (52);

[1] The subscript of x_1 may now be dropped.

i.e., equation (56) applies to *any* wave form. It is, also, obvious that exactly the same line of reasoning might be applied to a longitudinal wave, such as a sound wave, by replacing the transverse displacement of the string, here designated by y, by either the longitudinal displacement or by the pressure variation p in the sound wave. Thus, we might write,

$$\frac{\partial^2 p}{\partial t^2} = v^2 \frac{\partial^2 p}{\partial x^2} \tag{57}$$

for a sound wave, where p stands for the variation of pressure from normal.

It is instructive to derive the equation for the wave motion along a string which is not parallel to the x-axis.

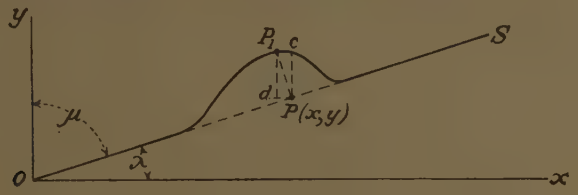

FIG. 14.

In Fig. 14, let the string OS be in the xy plane and make angles λ and μ with the axes. Let

$$\cos \lambda = l$$
$$\cos \mu = m$$

be the direction cosines. As in Fig. 13, let a disturbance travel along the string with velocity v. If P (coordinates x, y) is the position of any point on the string before displacement, and P_1 the position of the corresponding point after a displacement $D = PP_1$, we may write, as before, calling $OP = R$,

$$D = f(R)$$

where $f(R)$ is the f function of R.

For the equation of the wave motion corresponding to equation, (52) we may write,

$$D = f(R - vt) \tag{58}$$

It is preferable, however, to consider separately, the horizontal and the vertical components of D. Calling

$$D_x = Pd$$
$$D_y = Pc$$

We have

$$D_x = f_x(R - vt) \tag{59a}$$

$$D_y = f_y(R - vt) \tag{59b}$$

where f_x and f_y are suitable functions. Now,

$$\because OP = R = lx + my$$

$$\therefore D_x = f_x(lx + my - vt) \tag{60a}$$

$$D_y = f_y(lx + my - vt) \tag{60b}$$

Differentiate equation (60a) twice with respect to t, x, and y, in turn. We then have

$$\frac{\partial^2 D_x}{\partial t^2} = v^2 f_x''(lx + my - vt) \tag{61a}$$

$$\frac{\partial^2 D_x}{\partial x^2} = l^2 f_x''(lx + my - vt) \tag{61b}$$

$$\frac{\partial^2 D_x}{\partial y^2} = m^2 f_x''(lx + my - vt) \tag{61c}$$

Since $l^2 + m^2 = 1$, we have, by adding (b) and (c) of equations (61),

$$\frac{\partial^2 D_x}{\partial x^2} + \frac{\partial^2 D_x}{\partial y^2} = f_x''(lx + my - vt)$$

and, by substitution in equation (61a), this gives

$$\frac{\partial^2 D_x}{\partial t^2} = v^2 \left(\frac{\partial^2 D_x}{\partial x^2} + \frac{\partial^2 D_x}{\partial y^2} \right) \tag{62}$$

If the string be not confined to the xy plane but makes angles λ, μ, ν with the three coordinate axes x, y, and z, we should have, by an obvious extension of equation (62),

$$\frac{\partial^2 D_x}{\partial t^2} = v^2 \left(\frac{\partial^2 D_x}{\partial x^2} + \frac{\partial^2 D_x}{\partial y^2} + \frac{\partial^2 D_x}{\partial z^2} \right) \tag{63a}$$

and, for the other components of the displacement,

$$\frac{\partial^2 D_y}{\partial t^2} = v^2 \left(\frac{\partial^2 D_y}{\partial x^2} + \frac{\partial^2 D_y}{\partial y^2} + \frac{\partial^2 D_y}{\partial z^2} \right) \tag{63b}$$

$$\frac{\partial^2 D_z}{\partial t^2} = v^2 \left(\frac{\partial^2 D_z}{\partial x^2} + \frac{\partial^2 D_z}{\partial y^2} + \frac{\partial^2 D_z}{\partial z^2} \right) \tag{63c}$$

(e) Equations (63) are identical *in form* with equations (47) and (48), provided we put

$$v^2 = \frac{c^2}{\mu\epsilon}$$

Since equations (63) were derived from a wave motion, it is obvious *that equations* (47) *and* (48) *represent wave motions*, the

former an electric wave, the latter a magnetic wave, the *common* velocity of which is

$$v = \frac{c}{\sqrt{\mu\epsilon}} \tag{64}$$

In other words, just as the mechanical disturbance in the string (the displacement D in Fig. 14) was propagated along the string, so equations (47) tell us that an *electrostatic* disturbance in a medium is propagated through the medium with a velocity given by equation (64). And, similarly, for a magnetic disturbance.

7. The Electromagnetic Wave.—The differential equations of the electric wave (equations (47)) and those of the magnetic wave (equations (48)) seem to be independent of each other. But it must be recalled that they were derived by suitably combining the six equations (31) and (32) and that, therefore, they are not independent. The significance of this dependence, in so far as the wave motion is concerned, may be shown as follows: Consider a very large, plane, metal sheet, theoretically an infinite sheet, placed in coincidence with the yz plane. The sheet is represented in cross-section by the line ab in Fig. 15, the z-axis being perpendicular to the plane of the paper. Imagine a uniformly distributed, constant current flowing through this sheet parallel to the z-axis and flowing *toward* the reader. If the current be i_0' per centimeter of width of the sheet, it can be shown, by application of equation (9) to the infinite "current sheet," that there will be produced in the region adjacent to the sheet a magnetic field which will be in the y direction and which is given by[1]

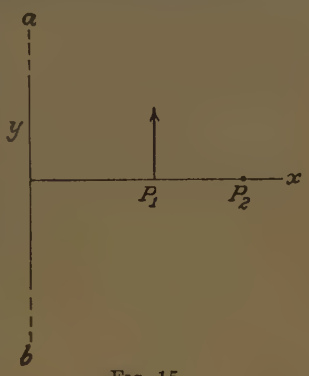

FIG. 15.

$$\beta = 2\pi i_0'$$

This field is represented at some point P_1 (Fig. 15). Now, allow the current through the sheet to vary at a rate $\partial i_0'/\partial t$. There will result a variation of β at a rate $\partial\beta/\partial t$ which rate, at any given instant, will vary from point to point along the x-axis because of the finite velocity of propagation of a magnetic disturbance (equation (64)).

[1] The derivation of this formula is left to the reader.

Let us now apply the electromagnetic equations (31) and (32) to this phenomenon. Since there are no x or z components of the magnetic field,

$$\alpha = \gamma = 0$$

and all their derivatives must be, also, zero; *i.e.*,

$$\frac{\partial \alpha}{\partial t} = \frac{\partial \alpha}{\partial y} = \frac{\partial \alpha}{\partial z} = 0$$

$$\frac{\partial \gamma}{\partial t} = \frac{\partial \gamma}{\partial x} = \frac{\partial \gamma}{\partial y} = 0$$

Further, because of the infinite extent of the current sheet in the yz plane, there can be no variation of *any* electric or magnetic quantity with y or z, since the events which happen at P_1 happen simultaneously at all points in a plane through P_1 parallel to the current sheet. We have, therefore,

$$\frac{\partial \beta}{\partial z} = 0$$

$$\frac{\partial Z}{\partial y} = \frac{\partial Y}{\partial z} = \frac{\partial X}{\partial z} = \frac{\partial X}{\partial y} = 0$$

Equations (31) and (32) thus become, respectively,

$$\frac{\epsilon}{c}\frac{\partial X}{\partial t} = 0 \tag{65a}$$

$$\frac{\epsilon}{c}\frac{\partial Y}{\partial t} = 0 \tag{65b}$$

$$\frac{\epsilon}{c}\frac{\partial Z}{\partial t} = \frac{\partial \beta}{\partial x} \tag{65c}$$

and

$$0 = 0 \tag{66a}$$

$$\frac{\mu}{c}\frac{\partial \beta}{\partial t} = \frac{\partial Z}{\partial x} \tag{66b}$$

$$0 = \frac{\partial Y}{\partial x} \tag{66c}$$

Differentiating equation (66b) with respect to t and equation (65c) with respect to x, and combining, we have

$$\frac{\partial^2 \beta}{\partial t^2} = \frac{c^2}{\mu\epsilon} \cdot \frac{\partial^2 \beta}{\partial x^2} \tag{67}$$

And differentiating equation (65c) with respect to t and equation (66b) with respect to x, we have

$$\frac{\partial^2 Z}{\partial t^2} = \frac{c^2}{\mu\epsilon}\frac{\partial^2 Z}{\partial x^2} \tag{68}$$

Equation (67) shows that we have a transverse *magnetic* disturbance traveling *in the x direction* with a velocity $\frac{c}{\sqrt{\mu\epsilon}}$; and equation (68) shows that *accompanying this magnetic disturbance is a transverse electric disturbance, also traveling in the x direction with the same velocity.* Further, the vectors in these disturbances

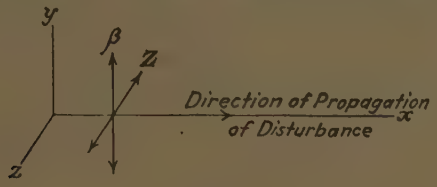

FIG. 16.

or waves, *i.e.*, β and Z, respectively, are *perpendicular* to each other, as well as to the direction of propagation (Fig. 16). These two mutually dependent waves constitute *a plane-polarized electromagnetic wave.*

8. Flow of Energy in an Electromagnetic Wave.—(*a*) Consider the direct current discussed in connection with Fig. 15 to be

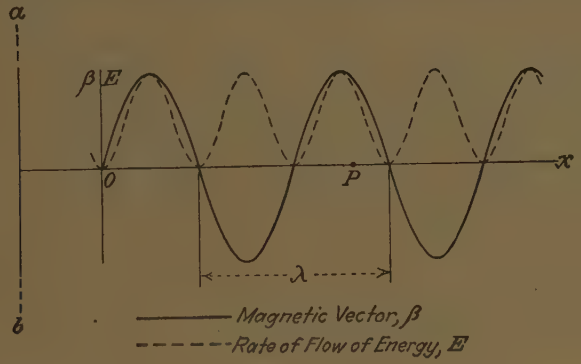

FIG. 17.

replaced by an alternating current. As before, let the infinite current sheet *ab* (Fig. 17) be coincident with the *yz* plane, and assume that the current in the sheet is represented by the usual sine function of the form

$$i'_0 = I'_0 \sin \frac{2\pi}{T} t$$

where T is the period of the alternating current, I'_0 is its amplitude and i'_0 is its value at time t, per unit width of the sheet.

The fluctuations of the magnetic field β in the neighborhood will be periodic with those of the current, and we may write for the value of β at some point O, arbitrarily located on the x-axis,

$$\beta = \beta_0 \sin \frac{2\pi}{T} t \tag{69}$$

where β_0 is the *amplitude* of β.[1] On account of the finite velocity of propagation of an electromagnetic disturbance, namely:

$$v = \frac{c}{\sqrt{\mu\epsilon}} \tag{70}$$

whatever happens at O will happen at some point P a little later. If we take O as the origin of coordinates, then $OP = x$, and the time required for a disturbance to pass from O to P will be x/v. By subtracting this time interval x/v from t of equation (69), we can express the variation of β at any point P on the x-axis by

$$\beta = \beta_0 \sin \frac{2\pi}{T}\left(t - \frac{x}{v}\right) \tag{71}$$

This is the equation of a plane-polarized magnetic wave train moving in the positive direction of x. If we fix our attention on a particular point, *i.e.*, if we keep x constant, then this equation shows that β is a simple harmonic function of t. If, however, we take a "snapshot" of the conditions along the x-axis at any instant, *i.e.*, if we keep t constant and vary x, the value of β is seen to be a simple harmonic function of x, as shown in the full line of Fig. 17. Starting from $x = 0$, the values of β are seen to be identical at the points $x = 0$, $x = vT$, $x = 2vT$, $x = 3vT$, etc., as may be shown by substituting these successive values of x in equation (71). The distance between these points is called a wave length, λ, *i.e.*, $vT = \lambda$, and an alternative form of equation (71) is

$$\beta = \beta_0 \sin 2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right) \tag{72}$$

(*b*) We may derive the equation of the accompanying electric wave as follows: We have seen (equations (67) and (68)) that we have to deal only with the Z component of the electric force. Differentiating equation (71) with respect to x gives

$$\frac{\partial\beta}{\partial x} = -\frac{1}{v}\frac{2\pi}{T}\beta_0 \cos \frac{2\pi}{T}\left(t - \frac{x}{v}\right) \tag{73}$$

[1] Strictly speaking, there is a phase difference between equation (69) and the preceding equation.

Putting this value of $\partial\beta/\partial x$ in equation (65c) gives

$$\frac{\epsilon}{c}\frac{\partial Z}{\partial t} = -\frac{1}{v}\frac{2\pi}{T}\beta_0 \cos\frac{2\pi}{T}\left(t - \frac{x}{v}\right) \tag{74}$$

Integrating this equation and remembering that the constant of integration must be zero, since it is assumed that there are no permanent fields, we have[1]

$$Z = -\frac{c}{\epsilon v}\beta_0 \sin\frac{2\pi}{T}\left(t - \frac{x}{v}\right) \tag{75}$$

$$= Z_0 \sin\frac{2\pi}{T}\left(t - \frac{x}{v}\right) \tag{76}$$

by putting

$$Z_0 = -\frac{c}{\epsilon v}\beta_0$$

A comparison of equations (76) and (71) shows that the electric wave is everywhere in phase with the magnetic wave.

(*c*) The magnitudes of the vectors β and Z are very closely related. Inserting the value of β from equation (71) into equation (75) gives

$$Z = -\frac{c}{\epsilon v}\beta \tag{77}$$

which shows that the two vectors are proportional to each other. A symmetrical relation between Z and β may be obtained by putting into equation (77) the value of c from equation (70). We then obtain.

$$\sqrt{\epsilon}\, Z = -\sqrt{\mu}\,\beta \tag{78}$$

If we are dealing with empty space, for which ϵ and μ are unity, *Z is numerically equal to β.*

(*d*) Now, the setting up of either an electric or a magnetic field involves energy, and it may be shown that the *energy per unit volume* in an electric field of strength F is

$$\frac{\epsilon F^2}{8\pi}$$

and in a magnetic field of strength H is

$$\frac{\mu H^2}{8\pi}$$

[1] The reader will find it instructive to consider the origin and the significance of the minus sign which appears before the right hand member of equation (75) and certain of the following equations.

Squaring both sides of equation (78) and dividing by 8π gives

$$\frac{\epsilon Z^2}{8\pi} = \frac{\mu\beta^2}{8\pi} \tag{79}$$

These two terms give, respectively, the electric and the magnetic energy per unit volume at any point in the wave where the fields are Z and β. It is, therefore, seen that the energy carried by the electric wave is equal to that carried by the magnetic wave, and the *total* energy w per unit volume at the point may be written, variously, as

$$w = \frac{\epsilon Z^2}{4\pi} = \frac{\mu\beta^2}{4\pi} = -\frac{\sqrt{\mu\epsilon}}{4\pi} Z\beta \tag{80}$$

This leads to an important theorem regarding the flow of energy in an electromagnetic wave. Consider an elementary volume, located, say, at P (Fig. 17) with faces of unit area and of thickness dx, placed parallel to the yz plane. Such an element of volume is shown in Fig. 18. By equation (80), the electromagnetic energy dW in this element of volume is, since the volume is dx,

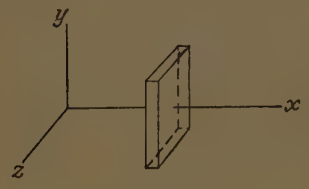

FIG. 18.

$$dW = -\frac{\sqrt{\mu\epsilon}}{4\pi} Z\beta dx \tag{81}$$

Since the wave moves to the right with velocity v, in a time dt given by

$$dt = \frac{dx}{v}$$

all this energy dW will have passed through the right-hand face. The *rate* of flow of energy through this (*unit*) area is, therefore,

$$\begin{aligned} \frac{dW}{dt} &= -\frac{\frac{\sqrt{\mu\epsilon}}{4\pi} Z\beta dx}{dx/v} \\ &= -\frac{v\sqrt{\mu\epsilon}}{4\pi} Z\beta \\ &= -\frac{c}{4\pi} Z\beta \end{aligned} \tag{82}$$

by equation (70). This is *Poynting's theorem*, and it states that in an electromagnetic wave (of the type herein discussed) the rate of flow of energy per unit area is proportional to the product of the electric and the magnetic vectors.

If, in equation (82), we put the value of Z given by equation (77), we get

$$\frac{dW}{dt} = \frac{c^2}{4\pi\epsilon v}\beta^2 \qquad (83)$$

$$= \frac{c^2}{4\pi\epsilon v}\beta_0^2 \sin^2 \frac{2\pi}{T}\left(t - \frac{x}{v}\right) \qquad (84)$$

Equation (83) shows that, irrespective of the sign of β, the flow of energy is always in the same direction, since β^2 is always positive. And equation (84) shows the variation of this energy flow with both t and x. Thus, considering the flow of energy through the slab in Fig. 18, *i.e.*, keeping x constant in equation (84), the rate of flow varies between the minimum rate zero and the maximum rate $\frac{c^2\beta_0^2}{4\pi\epsilon v}$. Or, considering the rate of flow, at any given instant at various points along the x-axis, we have the rate of flow given by the dotted curve in Fig. 17.

(*e*) Equation (84) gives the *instantaneous* rate of flow of energy through a square centimeter at right angles to the direction of propagation of the wave. A quantity of greater importance is the *average* rate of flow of energy. This corresponds to what is ordinarily called the *intensity* I of the wave, *i.e.*, the energy transferred per second per square centimeter of wave front. The average rate of flow of energy may readily be determined as follows: If one integrates equation (84) over a half-period, one has the total quantity of energy flowing through the square centimeter in time $T/2$. This quantity of energy divided by $T/2$ gives the desired average rate of flow. The graph of equation (84) is shown in Fig. 19 from a time $a = 0$ to a time $b = T/2$. Designating the average rate of flow per square centimeter by I, we may indicate the desired integration by

FIG. 19.

$$I = \frac{1}{T/2}\int_0^{T/2} \frac{dW}{dt}\, dt$$

$$= \frac{1}{T/2}\frac{c^2}{4\pi\epsilon v}\beta_0^2 \int_0^{T/2} \sin^2 \frac{2\pi}{T}\left(t - \frac{x}{v}\right) dt \qquad (85)$$

In this integration, x is kept constant. The value of the integral of equation (85) can be readily shown to be[1]

$$\frac{T}{4}$$

Putting this value of the integral in equation (85) gives

$$I = \frac{1}{8\pi}\frac{c^2}{\epsilon v}\beta_0^2 \tag{86}$$

Remembering that β_0 is the amplitude of the magnetic vector, we have, from this equation, the very important relation that *the intensity of an electromagnetic wave is proportional to the square of the amplitude of either the magnetic or the electric vector*, since, by equation (77), the latter are proportional to each other.

Applying equation (86) to empty space, for which $\epsilon = 1$, and $v = c$, we have

$$I = \frac{c}{8\pi}\beta_0^2$$

From definition, I is the energy contained in a train of electromagnetic waves comprising a column 1 sq. cm. in cross-section and c cm. long. The (average) energy[2] per cubic centimeter (or, more generally, per unit volume) in this wave train is $I/c = \beta_0^2/8\pi$. This quantity is called the *energy density* of the radiation. We shall discuss it later in Chap. VII.

9. The Electromagnetic Theory of Light.—Equation (64)

$$v = \frac{c}{\sqrt{\mu\epsilon}}$$

makes it possible to compute the velocity v of an electromagnetic wave in any medium from the constants μ and ϵ of the medium and the ratio c of the electrostatic to the electromagnetic system of electrical units. As stated on page 82, measurements show that $c = 3 \times 10^{10}$, cm. per second, very nearly. Considering *empty space*, for which both μ and ϵ are, by definition, unity, we have

$$v = c = 3 \times 10^{10} \text{ cm. sec.}^{-1} \tag{87}$$

[1] This is, at once, seen, since the average value of the integral $\int \sin^2\theta d\theta$ from $\theta = 0$ to $\theta = \pi$ is $\frac{1}{2}$. Or the equation may be integrated directly by setting $\psi = \frac{2\pi}{T}\left(t - \frac{x}{v}\right) = \frac{2\pi}{T}t - \phi$, where $\phi = \frac{2\pi}{T}\frac{x}{v} = \text{const.}$ Then $dt = \frac{T}{2\pi}d\psi$; and the limits of integration, 0 and $\frac{T}{2}$, become, respectively, $-\phi$ and $(\pi - \phi)$.

[2] It is to be remembered that half of this energy is due to the electric vector and half to the magnetic vector.

That is, *the velocity of an electromagnetic wave in empty space is equal to the ratio c between the electromagnetic and the electrostatic systems of units*, and has a numerical value of very nearly 3×10^{10} cm. sec^{-1}.

Now, numerous measurements have been made of the velocity of *light* in empty space:

	Velocity Cm. $sec.^{-1}$
Römer (1676)	2.92×10^{10}
Fizeau (1849)	3.13×10^{10}
Foucault (1862)	2.986×10^{10}
Cornu (1874)	3.004×10^{10}
Michelson (1879)	2.999×10^{10}
Michelson (1882)	2.998×10^{10}
Michelson (1926)[1]	2.99796×10^{10}

[1] *Astrophys. Jour.*, vol. 65, p. 1 (January, 1927).

The velocity of light is, thus, seen to be, *within experimental error*, equal to the velocity of electromagnetic waves. Further, as the phenomenon of polarization shows, light, in common with electromagnetic waves, is a *transverse* phenomenon. These two coincidences alone gave very strong support to the theory, first announced by Maxwell, in 1865, that light is an electromagnetic phenomenon; and that light consists of electromagnetic (instead of mechanical) vibrations, or waves, in the "ether"—a concept which at once removed many of the difficulties of the mechanical theory of the ether and of light vibrations, while retaining practically all the advantages of the older wave theory. If this identity be correct, all of the equations and principles discussed in this chapter should apply to light. For example, a beam of plane-polarized light should be composed of electric and magnetic vibrations at right angles to each other. Further, since electric and magnetic fields are continuous, the flow of energy in a light wave should be *continuous* over the *entire* wave front, and the *intensity* of the light wave should be proportional to the square of the amplitude (of either the electric or the magnetic vector, equation (86)), in agreement with the older theory.

The electromagnetic theory of light predicts, at once, the electrical nature of matter. For, as we have seen, electromagnetic waves originate as a result of the vibrating motion or, more generally, the *periodic* motion, of electric charges (*e.g.*, the alternating current in Fig. 17). If light waves be electromagnetic, they must have an electromagnetic origin. Now, the

facts of spectroscopy show that each element has a characteristic line spectrum, which, it must be assumed, originates in the atoms of the element. The conclusion is very direct, therefore, that the atoms must contain electric charges the vibrations of which send out light waves. We shall see, later, that this conclusion regarding the electrical nature of matter was supported by the application of the electromagnetic theory to other phenomena.

In the discussion in Sec. 8, we considered, for the sake of mathematical simplicity, the effect which would be produced by an alternating current sheet of infinite extent. The general nature of the phenomena would not, however, be changed if, instead of the infinite sheet, we had considered a wire, coincident with the z-axis, through which the alternating current was flowing. We should, then, have had a cylindrical wave spreading out from the wire as an axis. (This is the modern wireless antenna.) Indeed, a single electron, vibrating back and forth along, say, the z-axis, would send out a train of electromagnetic waves, *i.e.*, *would radiate energy*. We are, thus, led to a very profound and far-reaching generalization of the electromagnetic theory: namely, that *any accelerated charge must radiate energy in the form of an electromagnetic pulse or wave train.* If the charge, initially at rest, is given a *positive* acceleration; or if, in motion, it is given a negative acceleration (*i.e.*, is brought to rest), a single electromagnetic *pulse* is sent out—analogous to the sound pulse or "crack" sent out when a steel ball collides with a massive steel plate. If the acceleration be such that the charge vibrates back and forth over a linear path, or moves at uniform speed around a circular path, a *train* of waves is given out—analogous to the sound waves sent out by a vibrating tuning fork. *According to the electromagnetic theory, the acceleration of a charge cannot take place without this radiation of energy.* We shall frequently return to this point later.

10. The Discovery of Electromagnetic Waves.—The electromagnetic waves predicted by Maxwell were not demonstrated experimentally during his lifetime. The concept rested on purely theoretical foundations and on indirect evidence, until the work of Hertz in 1887–1888. A description of Hertz's experiments is beyond the scope of this book. The reader is referred to any one of the numerous accounts. Suffice it to say here, that Hertz produced electrical oscillations by taking advantage of the vibratory nature of the electric discharge discovered by

Henry. The frequency of the oscillations in Hertz's apparatus was of the order of 10^8 vibrations per second, giving rise to waves a few meters long. He detected the existence of these waves by means of a *resonator* consisting of a piece of wire, with polished brass balls on its ends, bent into the form of a circular loop so as to leave a small air gap between the knobs. The size of the loop was so adjusted that the natural period of the electrical oscillations of the loop would just coincide with the period of the "sending" apparatus.

Hertz proved conclusively that the oscillating discharge would produce electromagnetic waves, exactly as predicted by Maxwell, and that these waves had many, if not all, the properties of light waves: They could be reflected and refracted; they could be made to interfere and to produce stationery waves; and they were polarized.

Later, after the technique of producing and working with these waves had been developed, mainly by Hertz, their velocity was measured by various observers, with the following results:

Observers	Date	Velocity, centimeter-seconds^{-1}
Trowbridge and Duane...	1895	3.003×10^{10}
Saunders.....	1897	2.997×10^{10}
MacLean.....	1899	2.991×10^{10}

This velocity is seen to be identical with the velocity of light and, as predicted by Maxwell, is exactly equal to the ratio c of the two systems of electrical units. Maxwell's electromagnetic *theory* had become an experimental *reality*.

11. The Refraction of Light.—Indirect evidence rapidly accumulated to confirm the electromagnetic theory, and it proved very fruitful in predicting new phenomena. A few of these will be mentioned briefly.

Equation (64), $v = c/\sqrt{\mu\epsilon}$, gives the velocity of an electromagnetic wave and, therefore, also, if the electromagnetic theory of *light* be correct, the velocity of a light wave, in any medium for which the permeability μ and the dielectric constant ϵ are known. Now, the index of refraction n of a medium is given by

$$n = \frac{v_0}{v} \tag{88}$$

where v_0 is the velocity of light *in vacuo* and v is the velocity in the medium. For a vacuum $\mu = \epsilon = 1$, and, therefore, according to equation (64),

$$v_0 = c$$

For practically all transparent substances, $\mu = 1$, very nearly Therefore, for such substances,

$$v = \frac{c}{\sqrt{\epsilon}}$$

Substituting these values of v_0 and v in equation (88) gives

$$n = \sqrt{\epsilon} \tag{89}$$

That is, the index of refraction of a medium (for which the permeability is unity) should be equal to the square root of its dielectric constant. This prediction of the electromagnetic theory may be tested by direct experiment. The following tables give comparative data for certain illustrative substances, the index of refraction being for yellow light, and the dielectric constant being for room temperature, except as otherwise indicated, and for either direct currents or for alternating currents of low frequency.

TABLE I.—GASES

Substance	n	$\sqrt{\epsilon}$
H_2	1.000138	1.000132
Air	1.000294	1.000295
CO	1.000346	1.000345
CH_4	1.00044	1.00047
CO_2	1.000449	1.000473
N_2O	1.000503	1.000497
CS_2	1.00150	1.00145
NH_3	1.00038[1]	1.0039[1]
SO_2	1.00066[1]	1.0048[1]

[1]Note the number of zeros.

TABLE II.—LIQUIDS

Substance	n	$\sqrt{\epsilon}$
Benzene	1.50	1.51
Turpentine	1.49	1.46–1.51
Toluene	1.49	1.48–1.55
Petroleum	1.39	1.39

TABLE III.—LIQUEFIED GASES

Substance	n	$\sqrt{\epsilon}$
N_2O (15°C)	1.19	1.23
CO_2 (15°C.)	1.19	1.23
O_2 (−180°C.)	1.22	1.33
NH_3 (14°C.)	1.32	4.01

TABLE IV.—LIQUIDS

Substance	n	$\sqrt{\epsilon}$
Carbon disulphide	1.64	1.62
Ethyl ether	1.35	2.17
Phenol	1.54	3.10
Amyl alcohol	1.95	4.00
Acetone	1.36	4.55
Methyl alcohol	1.33	5.6
Glycerine	1.47	7.5
Water	1.33	8.9

TABLE V.—SOLIDS

Substance	n	$\sqrt{\epsilon}$
Paraffin	1.42	1.52
Quartz	1.55	2.12
Rock salt	1.54	2.42
Glass (crown)	1.53	2.64
Selenium	2.93	2.73

An examination of these data shows (1) that the agreement between n and $\sqrt{\epsilon}$ is exceptionally good for most gases (Table I); (2) that the agreement is fair for certain liquid hydrocarbons (Table II); (3) but that, for most liquids and solids (Tables III, IV, V), the law does not hold even approximately, water being the most notable exception. In general, the index of refraction is less than the square root of the dielectric constant.

The fact that, in most gases, the predicted equality of n and $\sqrt{\epsilon}$ is observed indicates that the theory leading to this law is, at least in certain particulars, substantially correct; while the disagreement found in the case of most liquids and solids indicates that the theory is incomplete—that certain factors have not been taken into account.

We do not have to seek far to find some of these factors. The data given above for the index of refraction n are for yellow light; while the values of the dielectric constant ϵ are for room temperatures and for frequencies which are either zero or are very low compared to the frequencies of light vibrations. Now, it is well known that the index of refraction depends on the wave length of the light and that the dielectric constant depends on both the temperature and the frequency of the alternating current used in the measurement. Thus, the index of refraction of quartz (ordinary ray) from the extreme ultra-violet to the far infra-red is shown in Table VI.

TABLE VI.—INDEX OF REFRACTION OF QUARTZ (ORDINARY RAY)

Wave length, centimeters	Index of refraction
0.185×10^{-4}	1.676
0.274	1.587
0.396	1.558
0.589	1.544
0.760	1.539
2.33	1.516
3.18	1.494
5.0	1.42
7.0	1.17

The variation of the dielectric constant of glycerin with frequency is given in Table VII.

TABLE VII.—THE VARIATION OF THE DIELECTRIC CONSTANT OF GLYCERIN WITH WAVE LENGTH

Frequency, sec.$^{-1}$	Equivalent wave length in vacuum, centimeters	Dielectric constant
0.25×10^8	1,200	56.2
1.50	200	39.1
4.00	7.5	25.4
35.0	8.5	4.4
750	0.4	2.6
5×10^{14}	(Yellow light)	$n^1 = 1.47$

[1] n = index of refraction.

The effect of temperature on dielectric constant is illustrated by the following data (Table VIII) for methyl alcohol.

TABLE VIII.[1]—THE VARIATION OF THE DIELECTRIC CONSTANT OF METHYL ALCOHOL WITH TEMPERATURE

Temperature, degrees centigrade	Dielectric constant
−100	58
50	45
0	35
50	31

[1] Data for Tables I to VIII were compiled from (1) LANDOLDT and BERNSTEIN: "Physikalische Tabellen" and (2) "The Smithsonian Physical Tables."

Even a casual inspection of Tables VI, VII, and VIII makes it obvious that one can compare values of the index of refraction and the square root of the dielectric constant only when the measurements are made under identical conditions. One can easily eliminate the effect of temperature by making the measurements of the two quantities at identical temperatures. And, likewise, the value of n is comparable with $\sqrt{\epsilon}$ only when the index of refraction is measured for a beam of radiation the frequency of which is equal to the frequency of the alternating current for which $\sqrt{\epsilon}$ is observed. An approach to such equality of conditions is to be found in the measurements on the index of refraction of water for electromagnetic waves the frequency of which is very low compared to that for ordinary light. Such measurements are given in Table IX.

TABLE IX.—INDEX OF REFRACTION OF WATER FOR ELECTROMAGNETIC WAVES[1]

Wave length, centimeters	Index of refraction
65	8.88
8.8	8.89
8.1	8.10
1.75	7.82

[1] Quoted by JEANS: "Electricity and Magnetism," p. 533.

The value of $\sqrt{\epsilon}$ for water is 8.94, which checks exceptionally well with the value of n for long waves. Again, the predictions of the electromagnetic theory are confirmed. But the question still remains: How is dispersion, *i.e.*, the variation of index of refraction with wave length, to be explained on the basis of the electromagnetic theory?

12. The Dispersion of Light.—The answer to the question raised at the end of the preceding section is to be found by considering the electrical nature of matter. It has been pointed out above that, if light be regarded as electromagnetic, we must look for the origin of light waves in the vibrations of electrical charges. Since matter under various conditions of excitation—high temperature, electrical discharge, etc.—sends out light waves, the implication is obvious that matter contains electrical charges or electrically charged bodies capable, *perhaps*, of vibrating with definite periods about certain fixed positions. The natural frequencies of these vibrations in unexcited matter, or, at least, some of them, might be expected to be of the order of magnitude of frequencies encountered in ordinary light. It might be expected, therefore, that the passage of light through matter would be materially influenced by these electrically charged particles, particularly if the frequency of the light happens to be near the natural frequency of vibration of the particles about their several positions of equilibrium. If, however, the frequency of the light is far removed from, say is very much less than, the natural frequency of the particles, we should expect the presence of the electrical charges in the matter to exert little or no effect on the passage of the light. This is the explanation of the fact, shown in Table IX, that the index of refraction for electromagnetic waves several centimeters long agrees so closely with the square root of the dielectric constant.

It would lead us too far afield to give even an elementary discussion of the phenomena of dispersion on the basis of the electromagnetic theory.[1] It may, however, be instructive to consider the way in which such a discussion may be started, so as to point out the modifications which have to be made in the fundamental electromagnetic equations.

In deriving equations (31), we considered the current density j to be made up solely of a "displacement" current $\frac{\epsilon}{4\pi}\frac{dF}{dt}$ due

[1] The reader is referred to an excellent discussion in HOUSTOUN: "Treatise on Light," Chap. XXIV.

to the change in the electric field F. If, however, the medium in which the change of field takes place contains electric charges, there will be an *actual* displacement of electricity which must be added to the quasi-displacement $\frac{\epsilon}{4\pi}\frac{dF}{dt}$ to get the total effective current density. Thus, consider a charge e occupying, in the absence of electric fields, an equilibrium position P_1 (Fig. 20). Imagine an electric field X, directed toward the right, to displace the charge to a position P_2 such that the force Xe is just balanced by a "return" force, say $f \cdot x$, where $x \equiv P_1P_2$ is the displacement and f is, for small displacements, a constant. That is,

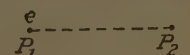

FIG. 20.

$$Xe = -fx$$

If X changes at a rate of dX/dt, then the position of the charge will change at some rate dx/dt, the magnitude of which will be determined by several factors, such as the mass m of the body containing the charge e, the value of f, etc. Now, let the medium contain N such "mobile" charges per unit volume. If, at any instant, these charges all have a velocity dx/dt, the rate of transfer of charge through unit area at right angles to dx/dt is

$$Ne\frac{dx}{dt}$$

The effective current density in this direction will, then, be given by

$$j_x = \frac{\epsilon}{4\pi}\frac{\partial X}{\partial t} + Ne\frac{dx}{dt} \tag{90}$$

instead of by the simpler equation (27). Introducing this new value of j_x into equation (21a), we have, instead of equation (31a), the relation

$$\frac{\epsilon}{c}\frac{\partial X}{\partial t} + \frac{4\pi}{c}Ne\frac{dx}{dt} = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} \tag{91}$$

This equation can be applied to the case of a light wave passing through the medium. X then becomes the periodically varying electric vector in the wave. Let ν be the frequency of the light vibrations, and let ν_0 be the natural frequency of vibration of the charged particles of the medium about their positions of equilibrium. It can, then, be shown[1] that the index of refrac-

[1] See HOUSTOUN: "Treatise on Light," *loc. cit.*

tion n of a medium which is transparent to the radiation of frequency ν is given by

$$n^2 = 1 + \frac{Ne^2}{\pi m(\nu_0^2 - \nu^2)} \tag{92}$$

N being, as before, the number of charged particles per unit volume, e the charge, and m the mass of each particle. This formula shows that the index of refraction should depend on the frequency of the light ν and on the natural frequency of vibration ν_0 of the charged particles. These charged particles are nowadays identified as electrons. There may be different groups of electrons in the medium. That is, we may have N_1 electrons per unit volume which have a natural frequency ν_1; N_2 electrons per unit volume with natural frequency ν_2; etc. We should then have

$$n^2 = 1 + \frac{N_1e^2}{\pi m(\nu_1^2 - \nu^2)} + \frac{N_2e^2}{\pi m(\nu_2^2 - \nu^2)} + \cdots \tag{93}$$

Or, to put the expression in more compact form, factoring $e^2/\pi m$, we may write

$$n^2 = 1 + \frac{e^2}{\pi m}\sum\frac{N}{(\nu_0^2 - \nu^2)} \tag{94}$$

This formula is similar to the well-known Sellmeier formula for dispersion, deduced by Sellmeier, about 1870, on the basis of the elastic solid theory of light.

TABLE X.—COMPARISON OF THE OBSERVED VALUES OF THE INDEX OF REFRACTION OF WATER THROUGH THE VISIBLE SPECTRUM WITH THOSE COMPUTED FROM EQUATION (92)

Wave length λ (*in vacuo*), centimeter	Frequency ν, sec.$^{-1}$	Index of refraction n	
		Observed[1]	Computed
0.7600×10^{-4}	0.3943×10^{15}	1.3293	.....
0.6870	0.4365	1.3309	1.3305
0.6563	0.4567	1.3317	1.3310
0.5893	0.5085	1.3335	1.3328
0.5270	0.5687	1.3358	1.3351
0.4861	0.6166	1.3377	1.3371
0.4308	0.6957	1.3412	1.3409
0.3968	0.7553	1.3441	.....

[1] Quoted by HOUSTOUN, *loc. cit.*

This dispersion formula represents, fairly well, the variation with frequency of the index of refraction of transparent bodies in

the visible part of the spectrum. For example, Table X shows, in the third column, the observed values of the index of refraction of water through the visible spectrum. Equation (92) may be put in the form

$$n^2 = 1 + \frac{B}{\nu_0^2 - \nu^2} \tag{95}$$

where $B = Ne^2/\pi m$. Forming a pair of simultaneous equations by substituting in equation (95) the corresponding values of ν

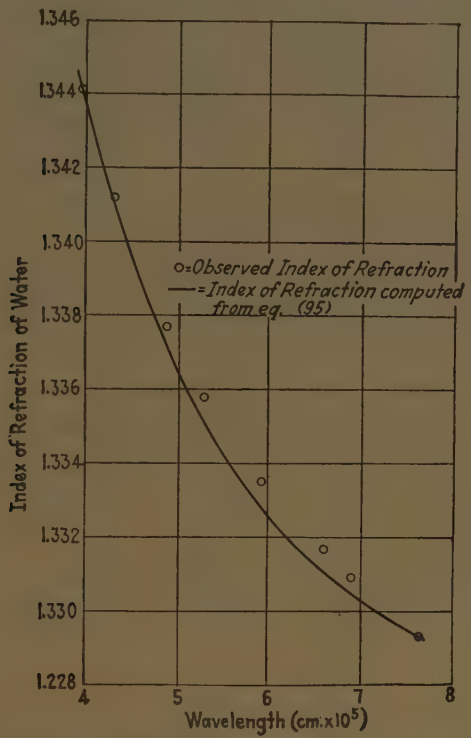

FIG. 21.—Comparison of observed values of index of refraction of water with the predictions of equation (95).

and n from the first and last lines, respectively, of Table X, one can determine the constants B and ν_0. One obtains, in this way,

$$B = 6.48 \times 10^{30}$$
$$\nu_0 = 2.93 \times 10^{15}$$

By putting these values of B and ν_0 back in the equation, the values of n for the other wave lengths are determined, as shown

in the fourth column of Table X. In Fig. 21, the full line gives the computed values of n, while the points give observed values. The agreement is seen to be fair.

In passing, a word may be said regarding the physical significance of the two constants ν_0 and B. As previously explained, ν_0 represents the natural frequency of the charged particles. The frequency $\nu_0 = 2.93 \times 10^{15}$ corresponds to the wave length (*in vacuo*) of 0.102×10^{-4} cm., which is in the extreme ultra-violet. If the theory be approximately correct, water must have particles, *i.e.*, electrons, with a natural frequency corresponding to a wave length somewhere in the extreme ultra-violet. If radiation of this wave length were to pass through water, the particles should resonate strongly, *i.e.*, the water should absorb this wave length. Or, in other words, the ν_0 of equations (92) and (94) corresponds to absorption bands. Water is known to have several absorption bands in the infra-red, and it absorbs in the ultra-violet. The complete dispersion formula should take account of these several frequencies, as is indicated by equation (94). A further modification must be introduced in the dispersion formula to take account of the effect of absorption in the medium. For these extensions, the reader is referred to any standard treatise on the electromagnetic theory of light.

Since $B = Ne^2/\pi m$, we are enabled to compute N, the number of "mobile" electrons per cubic centimeter of water, using data which we shall discuss later. Putting $B = 6.48 \times 10^{30}$; e (the electronic charge) $= 4.774 \times 10^{-10}$ e.s.u.; and m (the mass of the electron) $= 0.9 \times 10^{-27}$ gm., we have

$$N = 8 \times 10^{22} \text{ electrons per cubic centimeter}$$

It can be shown[1] that there are approximately 3.4×10^{22} molecules of water per cubic centimeter. In other words, approximately 2 electrons per molecule of water (*i.e.*, $8 \div 3.4 = 2.3$) have a natural period corresponding to a wave length in the

[1] The numerical value of Avogadro's constant, *i.e.*, the number of molecules in a gram-molecule, is 6.06×10^{23}. Since 1 gram-molecule of water contains 18 grams, there are $\frac{6.06}{18} \times 10^{23} = 3.37 \times 10^{22}$ molecules per gram of water, or per cubic centimeter, since the density of water is unity. As water undergoes thermal expansion, of course, the number N of electrons per cubic centimeter should change. Hence, the index of refraction should change with density, a conclusion in agreement with experiment.

ultra-violet, a conclusion which, if it be not rigorous, is, at least, reasonable.

13. Summary.—In the foregoing, we have attempted to sketch briefly some of the fundamentals and a few of the applications of the electromagnetic theory. We have seen that the electromagnetic waves, predicted by the theory, were observed experimentally by Hertz and have now passed far beyond the academic stage of theoretical and experimental science by virtue of their world-wide application in radio. When applied to light, we have seen that the electromagnetic theory satisfactorily accounts for polarization, refraction, and dispersion. Among the other phenomena of optics to which the electromagnetic theory has been, at least in part, successfully applied may be mentioned reflection, total reflection, the Zeeman effect, the Faraday rotation of the plane of polarization, and the optical properties of metals. If one is to estimate the value of a theory by its success in explaining and grouping together previously observed phenomena and in predicting new ones, there can be no doubt that the Electromagnetic Theory of Light ranks as the outstanding development of the nineteenth century.

It may be well to mention again two of the fundamental tenets of the electromagnetic theory, to which we shall have occasion to refer later. *First*, it is an inescapable conclusion from the theory, a conclusion, in fact, without which the whole theory falls, that an accelerated charge must send out an electromagnetic disturbance, *i.e.*, *must radiate energy*. It will be shown later, that the rate dW/dt of emission of energy by an accelerated charge is given by the equation

$$\frac{dW}{dt} = \frac{2}{3}\frac{Q^2\dot{g}^2}{c^3} \tag{96}$$

where Q is the charge, g its acceleration (positive or negative, g^2 being always positive), and c the velocity of light. *Second*, this rate of emission of energy, as well as the wave train which carries it, must be *continuous*. That is, if we imagine the wave front of our electromagnetic wave magnified indefinitely, it should still be continuous, should show no structure. For the wave is composed of magnetic and electric vectors which, so far as we know, have no structure and which may assume *any values whatever* from zero up. The concept of lines of electric or of magnetic force is, it must be remembered, simply a geometrical "picture" to help us keep in mind the various phenomena of electric and magnetic

fields. Lines of force have no physical significance *as lines*. The modern Quantum Theory, to the development of which we shall presently turn, comes into direct conflict with these two indispensable tenets of the electromagnetic theory.

Some References to the Electromagnetic Theory of Light

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CHAPTER V

SOME THEOREMS CONCERNING MOVING[1] CHARGES

1. The Magnetic Field Produced by a Moving Charge.—In his paper entitled "On the Magnetic Effect of Electric Convection," Prof. H. A. Rowland[2] proved conclusively *by experiment* that a moving charge produces a magnetic field. The idea had been suggested by both Faraday and Maxwell, but Rowland seems to have been the first to obtain experimental evidence of the effect. We can use the results of Sec. 6 of the previous chapter to determine the magnitude of the field produced by the motion of a charge.

Equation (27) Chap. IV, states that an electric field which is changing at a rate dF/dt is *equivalent* to a current of density j given by

$$j = \frac{1}{4\pi}\frac{dF}{dt}$$

(We shall restrict the discussion to cases where $\epsilon = 1$.) If the rate of change of field be uniform over an area S, taken, say perpendicular to F which, for simplicity, is assumed uniform over S, the equivalent current i through that area is given by

$$i = Sj = \frac{1}{4\pi}\frac{SdF}{dt} \tag{1}$$

But $S \cdot dF$ is the change of electric flux through the area, since, in the terminology of lines of electric flux, dF is the *change* in lines per unit area. Representing the total electric flux through the area S by Φ, we may write,[3]

[1] We shall limit the discussion in this chapter to cases where the velocity of the charge is small compared to the velocity of light.

[2] *Amer. Jour. Sci.*, vol. 15, p. 30 (1878). See also Papers No. 12 and No. 43 in the "Physical Papers of Henry A. Rowland."

[3] More generally,

$$i = \int j dS$$

where dS is an element of the surface S. Therefore,

$$i = \frac{1}{4\pi}\int \frac{dF}{dt} dS = \frac{1}{4\pi}\frac{d}{dt}\int dF \cdot dS = \frac{1}{4\pi}\frac{d\Phi}{dt}$$

since the total change of flux through S is the change of flux dF through unit area integrated over the whole area.

$$d\Phi = SdF$$

$$\therefore i = \frac{1}{4\pi}\frac{d\Phi}{dt} \qquad (2)$$

and by computing the rate of change $d\Phi/dt$ of the total flux through an area, we may determine, by equation (2), the equivalent current through the area.

Let a positive charge Q (Fig. 22) be moving with velocity v in the positive direction of X along the x-axis, the charge coinciding with the origin O at the instant shown. We wish to find the magnetic field H_P at the point P which is at a distance R from O. The line $OP(=R)$ makes an angle ϕ with the direction of motion of the charge. Describe about O a sphere of radius R and let PMP' represent a segment of the sphere the plane PNP' being perpendicular to the direction of motion and distant ON $(=x)$[1] from Q. If the velocity v be small compared to the velocity of light, there will be, symmetrically surrounding Q, $4\pi Q$ lines of force (more correctly, lines of induction).

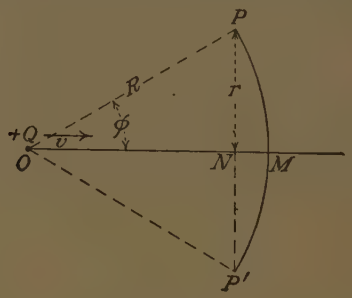

FIG. 22.

We shall compute the total number of these lines Φ_s which go through the surface PMP' and then the rate of change of Φ_s due to the motion of the charge. The field intensity F_s everywhere over the area PMP' is

$$F_s = \frac{Q}{R^2}$$

and the total flux Φ_s through PMP' is

$$\begin{aligned}\Phi_s &= F_s \times (\text{area } PMP') \\ &= \frac{Q}{R^2} \times 2\pi R^2(1 - \cos\phi) \\ &= 2\pi Q(1 - \cos\phi) \qquad (3)\end{aligned}$$

[1] Note that x is taken as the *distance* between Q and N; *i.e.*, x decreases as Q moves toward the right.

Now,

$$\cos \phi = \frac{x}{\sqrt{x^2 + r^2}}$$

where r $(=PN)$ is the radius of the base of the segment and $x = ON$. Therefore,

$$\Phi_s = 2\pi Q\left[1 - \frac{x}{(x^2 + r^2)^{\frac{1}{2}}}\right] \tag{4}$$

Differentiating both sides of equation (4) with respect to t and remembering that $-\frac{dx}{dt} = v$, we have

$$\frac{d\Phi_s}{dt} = 2\pi Q\left[(x^2 + r^2)^{-\frac{1}{2}} - x^2(x^2 + r^2)^{-\frac{3}{2}}\right] v$$

$$= \frac{2\pi Q v}{R}\left(1 - \frac{x^2}{R^2}\right)$$

by replacing $(x^2 + r^2)^{\frac{1}{2}}$ by R

Now, $\frac{x}{R} = \cos \phi$, and $\left(1 - \frac{x^2}{R^2}\right) = (1 - \cos^2 \phi) = \sin^2 \phi$

Therefore,

$$\frac{d\Phi_s}{dt} = \frac{2\pi Q v}{R} \sin^2 \phi \tag{5}$$

Therefore, by equation (2)

$$i_s = \frac{Qv}{2R} \sin^2 \phi \tag{6}$$

where i_s is the equivalent displacement current through the segment PMP'; incidentally, also, the same displacement current "flows" through the base of the segment PNP'.

So far as computing magnetic fields is concerned, we may treat this equivalent current i_s as if it were an actual current. Since the phenomena due to the motion of the charge along ON must be perfectly symmetrical around ON, the magnetic field produced at all points, such as P or P', on the circumference of the circle PNP' will be everywhere the same. Calling this field H_P (it is everywhere tangent to the circumference), the work W done in carrying a unit magnetic pole once around the circumference is

$$W = 2\pi r \cdot H_P \tag{7}$$

We may, also, compute the work W from the expression $W = 4\pi i_s$ (see equation (11), Chap. IV), *viz.*,

$$W = 4\pi \frac{Q'v}{2R} \sin^2 \phi \tag{8}$$

(Note that the quantities i'_s and Q' are now expressed in electromagnetic units.) Equating the right hand sides of equations (7) and (8) and solving for H_P, we have

$$H_P = \frac{Q'v}{R} \cdot \frac{\sin^2 \phi}{r}$$

$$= \frac{Q'v}{R} \cdot \frac{\sin \phi}{r} \cdot \frac{r}{R}$$

$$\therefore H_P = \frac{Q'v}{R^2} \sin \phi \tag{9}$$

since $\sin \phi = r/R$.

Equation (9) is the equation sought. It shows that the magnetic field H_P produced at any instant at a point P by a moving charge Q is (1) proportional to the velocity of the charge, (2) inversely proportional to the square of the distance R between the charge and the point, and (3) depends on the sine of the angle ϕ between the direction of motion and a line drawn from the point to the charge.

A word about units: In equation (8), Q' must be in electromagnetic units if W is to be in ergs, to conform to the usual units in which W is given in equation (7). That is, in equation (9), Q' must be in electromagnetic units to give H_P in gauss. If, as is frequently found convenient, one wishes to express the charge in electrostatic units, one must write,

$$H_P = \frac{1}{c} \frac{Qv}{R^2} \sin \phi \tag{10}$$

where c is the velocity of light.

It is to be observed that the field at all points on OM (*i.e.*, $\phi = 0$) is zero. The field is a maximum at points given by $\phi = \pi/2$. Comparing equation (9) with equation (8) Chap. IV, one observes that the moving charge behaves as if $Q'v$ were a "current element" $i' \cdot ds$.

2. The Force Acting on a Charge Moving in a Magnetic Field. Since H_P as determined by equation (9), is the strength of the magnetic field at P (Fig. 22), a magnetic pole of strength m placed at P would experience a force f_m perpendicular to the plane of the paper (toward the reader) given by

$$f_m = mH_P \tag{11}$$

By Newton's third law, the moving charge must experience a force f_Q *equal in magnitude and opposite in direction to* f_m; or,

$$f_Q = -mH_P = -m \frac{Q'v}{R^2} \sin \phi \tag{12}$$

Now, m/R^2 is the strength of the magnetic field H at O due to the pole m which we assumed placed at P. We may write, therefore (omitting the minus sign),

$$f_Q = HQ'v \sin \phi \tag{13}$$

where ϕ is now to be taken as the angle between the direction of motion of the charge and the direction of the field H through which the charge is moving.

There are many cases where the charge moves in a direction at right angles to the magnetic field. In this case, $\sin \phi = 1$, and we have

$$f_Q = HQ'v \tag{14}$$

f_Q being at right angles to both H and v. If the charge moves parallel to the field, $\sin \phi = 0$, and there is no force acting on the charge.

3. The Energy Contained in the Magnetic Field Surrounding a Moving Charge.—Consider a charge Q (electrostatic measure) uniformly distributed over the surface of a small sphere S of radius a (Fig. 23) and let S be moving in the direction Ox with a velocity v. Equation (10) shows that the magnetic field at some point P, the (polar) coordinates of which are ρ, θ, is given by

$$H_P = Qv \frac{\sin \theta}{c\rho^2} \tag{15}$$

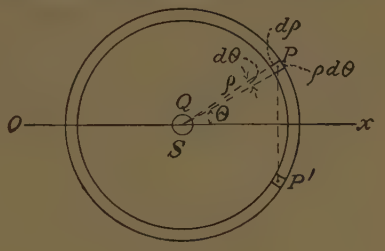

FIG. 23.

Now, the energy per unit volume in a magnetic field of strength H is $H^2/8\pi$. In an elementary volume dV including P, the energy dW is

$$dW = \frac{1}{8\pi} H_P^2 dV \tag{16}$$

Since the magnetic field is symmetrical around Ox, we may take as an elementary volume a ring the cross-section of which is $d\rho \cdot \rho d\theta$ and the length of which is $2\pi\rho \sin \theta$. We, thus, have

$$\begin{aligned} dV &= d\rho \cdot \rho d\theta \cdot 2\pi\rho \sin \theta \\ &= 2\pi\rho^2 \sin \theta d\rho d\theta \end{aligned} \tag{17}$$

Putting into equation (16) the value of H_P from equation (15) and the value of dV from equation (17), we obtain for dW,

$$dW = \frac{1}{4} \frac{Q^2v^2}{c^2} \frac{\sin^3 \theta}{\rho^2} d\rho d\theta \tag{18}$$

We can obtain the total energy W due to the magnetic field in the space surrounding the moving charge by integrating equation (18) between the limits[1] 0 and π for θ and between the limits a and ∞ for ρ, a being the radius of the sphere S. That is,

$$W = \frac{1}{4}\frac{Q^2v^2}{c^2}\int_a^\infty \int_0^\pi \frac{\sin^3\theta}{\rho^2} d\rho d\theta \tag{19}$$

$$\therefore W = \frac{1}{3}\frac{Q^2v^2}{c^2}\int_a^\infty \frac{d\rho}{\rho^2} \; * \tag{20}$$

Integrating equation (20) with respect to ρ and putting in the limits gives

$$W = \frac{1}{3}\frac{Q^2v^2}{ac^2} \tag{21}$$

Thus, W is proportional to the square of the velocity of the charged body; and the charge behaves as if *it* had mass, since this energy W is quite independent of any kinetic energy which the sphere itself may have. We may write equation (21):

$$W = \frac{1}{2}\cdot\frac{2}{3}\frac{Q^2}{ac^2}v^2$$

which, by comparison with the well known expression for kinetic energy, $\frac{1}{2}mv^2$, indicates that the equivalent mass m_Q of the charge Q is given by

$$m_Q = \frac{2}{3}\frac{Q^2}{ac^2} \tag{22}$$

This equivalent mass is seen to be inversely proportional to the radius a of the sphere. (Note that Q is measured in e.s.u.)

4. The Energy Radiated by an Accelerated Charge.—Consider a "point" charge initially at rest at O (Fig. 24). Let the charge be given an acceleration g for a short time τ, during which time the charge reaches P_1, its velocity v at P_1 in the direction Ox being given by

$$v = g\cdot\tau, \tag{23}$$

v being small compared to the velocity of light. After an additional time t, *large compared to the interval* τ, the charge now traveling with *uniform*[2] velocity v will have reached some point

[1] This integration gives the energy in a shell of radius ρ and of thickness $d\rho$.

* $\int_0^\pi \sin^3\theta d\theta = \left[\frac{\cos^3\theta}{3} - \cos\theta\right]_0^\pi = \frac{4}{3}$.

[2] Irrespective of the inertia of any material matter with which the moving charge may be associated, the charge has inertia by virtue of the magnetic field set up by its velocity, as explained in the preceding section.

P_2, where $P_1P_2 = vt$. Let ONL represent any line of force from the charge while stationary at O. The disturbance due to starting the charge will travel outward along this line of force with the velocity of light c. Outside a sphere of radius $c(\tau + t)$ concentric about O the field will not have received "news" of the motion of the charge and will, therefore, be radial from O, as shown by the line NL. *Inside* a sphere of radius ct concentric about P_2 the field will be radial from P_2, as shown by the line P_2M. Between these two spheres will be a shell within which the transition from the one field to the other occurs. The transition is shown by the line MN, and, at the instant represented, *i.e.*,

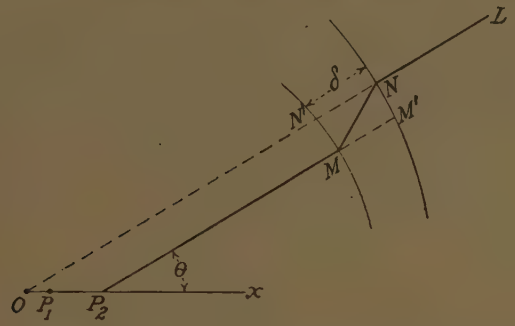

FIG. 24.—Diagrammatic representation of the origin of an ether pulse.

$(\tau + t)$ seconds after starting, the line of force formerly occupying the position ONL is now given by P_2MNL, the "break" MN traveling outward with velocity c. It will very much simplify the discussion to make the assumption that the points O, P_1, and P_2 are so close together as, practically, to be coincident. The two spheres are, then, concentric, and the shell has a uniform thickness $\delta = c\tau$. This is justified if $v << c$, and if $\tau << t$. Then,

$$OP_2 = vt$$

very nearly.

This spherical shell is an electromagnetic wave, or pulse, originating as a result of the acceleration given to the charge. The line MN represents the direction of the field within the pulse. We have, for simplicity, represented MN as a straight line. Its shape will depend on the nature of the acceleration given to g. The generality of the discussion, however, is not lessened by assuming that MN is straight, since, if MN be not straight, we may divide the shell up into a large number of

elementary shells within each of which the intercepted portion will be straight. Let Fig. 25 represent, to a larger scale, a portion of the shell in the neighborhood of MN, in Fig. 24. Let the direction and intensity of the electric field, within the shell at this point, be represented by F. We may resolve F into components F_T tangential to the surfaces of the shell, and F_P perpendicular to these surfaces. From Fig. 25, it is obvious that

$$\frac{F_T}{F_P} = \frac{MN'}{MM'} \tag{24}$$

But

$$MM' = \delta = c\tau, \tag{25}$$

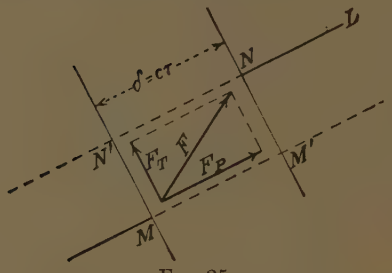

FIG. 25.

δ being the thickness of the shell, and τ the duration of the acceleration given to the charge. Also

$$MN' = OP_2 \sin\theta = vt \sin\theta \tag{26}$$

(see Fig. 24), subject to the limitations previously mentioned. Therefore,

$$\frac{F_T}{F_P} = \frac{vt \sin\theta}{\delta} \tag{27}$$

Now, F_P, the component of the field within the shell and perpendicular to the surfaces of the shell, must be exactly given by

$$F_P = \frac{Q}{R^2} \tag{28}$$

where R is the radius of the shell. This is readily seen, since every line of force such as P_2M (Fig. 24) has an extension MM'. Combining equations (27) and (28), we have

$$F_T = \frac{Qvt}{\delta R^2} \sin\theta$$

$$= \frac{Qv}{c\delta R} \sin\theta \tag{29}$$

since $R = ct$, approximately.

We may now regard the field surrounding the moving charge as practically equivalent to a constant radial field moving at uniform velocity with the charge, upon which is superimposed a tangential field F_P which moves radially outward with the velocity of light. This tangential component, therefore, we may consider as constituting the *electric* vector in an electromagnetic wave, *associated with which must be*, as we saw in Chap. IV, *a magnetic vector* H_T (perpendicular to the plane of the paper). The energy per unit volume, ω, within the pulse due to these two vectors is

$$\omega = \frac{F_T^2}{8\pi} + \frac{H_T^2}{8\pi}$$

or, since we have seen, in Chap. IV, that the energy associated with the electric vector in an electromagnetic wave is exactly equal to the energy associated with the magnetic vector, we may write

$$\omega = \frac{F_T^2}{4\pi}$$

By equation (29),

$$\omega = \frac{1}{4\pi} \frac{Q^2 v^2}{c^2 R^2 \delta^2} \sin^2 \theta$$

If we assume that ω is constant from front to back of the pulse, the "intensity" I of the pulse, *i.e.*, the energy per unit area of pulse surface, is

$$I = \omega\delta = \frac{1}{4\pi} \cdot \frac{Q^2 v^2}{c^2 R^2 \delta} \sin^2 \theta \qquad (30)$$

We, thus, see (1) that the intensity of the pulse is inversely proportional to R^2 (the well known inverse-square law of radiation); (2) inversely proportional to the thickness of the pulse; and (3) is zero in the direction of motion of the charge ($\sin \theta = 0$) and greatest at right angles to this direction. The total energy W contained in the pulse is determined by integrating this intensity over the entire surface of the pulse, *i.e.*,

$$W = \int I dS \qquad (31)$$

where dS is a surface element of the pulse.

This integration is readily performed. The spherical pulse, radius R, is represented, in Fig. 26, with its center at O. Since the phenomenon is symmetrical about Ox, the direction of motion, we may take as a surface element dS of the sphere a

narrow zone centered at P, the width of the zone being $R \cdot d\theta$ and its length $2\pi R \sin \theta$. Therefore,

$$\begin{aligned} dS &= 2\pi R \sin \theta \cdot R d\theta \\ &= 2\pi R^2 \sin \theta \, d\theta \end{aligned} \tag{32}$$

Using equations (30) and (32), we may write, for equation (31),

$$W = \frac{1}{2} \frac{Q^2 v^2}{c^2 \delta} \int_0^{\pi} \sin^3 \theta d\theta \tag{33}$$

$$\therefore W = \frac{2}{3} \frac{Q^2 v^2}{c^2 \delta} \tag{34}$$

The energy of the pulse is, therefore, inversely proportional to its thickness.

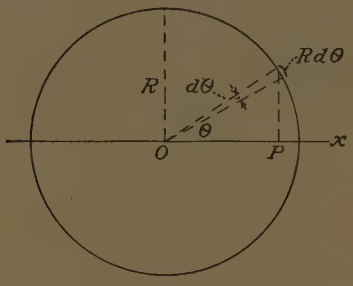

FIG. 26.

Now, assuming that the acceleration g which the charge experienced was uniform, $v = g \cdot \tau$; also, $\delta = c\tau$. We may, therefore, write equation (34):

$$W = \frac{2}{3} \frac{Q^2 g^2}{c^3} \tau \tag{35}$$

This important equation gives the total quantity of energy radiated as a result of the acceleration given to the charge for a time τ. It leads, at once, to a still more important relation, namely, the rate of radiation of energy dW/dt as a function of the acceleration given to the charge.[1] Thus,

$$\frac{dW}{dt} = \frac{W}{\tau} = \frac{2}{3} \frac{Q^2 g^2}{c^3} \tag{36}$$

[1] Strictly speaking, W/τ gives the *average* rate of radiation of energy during the time τ. But the same result would be obtained by a more rigorous discussion in which τ is divided up into a large number n of time elements $d\tau$ and the shell or pulse into a corresponding number of elements of thickness $d\delta$. It can readily be seen that a *uniform* acceleration g would *not* result in a straight line MN (Fig. 24).

It is to be noted that, irrespective of whether g is positive or negative, g^2 *is always positive;* therefore, *an accelerated charge radiates energy whether the acceleration be positive or negative.* As stated at the end of Chap. IV, *this is a necessary and an unambiguous conclusion from the electromagnetic theory.* It explains why a vibrating electron should radiate electromagnetic waves—the mechanism of the classical theory of light production. It explains why a swiftly moving electron, when suddenly stopped by collision, say with the target of an X-ray tube, should send out an "ether pulse," which was an early theory of the process of the production of X-rays.

5. Some Special Cases of Radiation by Accelerated Charges.—It may be of interest to consider one or two applications of the discussion in the preceding section.

First, to determine the ratio of the energy W_r radiated, when a charge Q moving with velocity v is brought to rest, to the energy W_m in the magnetic field initially surrounding the moving charge: From equation (34),

$$W_r = \frac{2}{3}\frac{Q^2v^2}{c^2\delta}$$

This applies to the case either of a charge starting from rest and acquiring a velocity v or to a charge initially moving with velocity v being brought to rest. From equation (21), the magnetic energy W_m associated with a charge moving with velocity v is

$$W_m = \frac{1}{3}\frac{Q^2v^2}{ac^2}$$

Therefore,

$$\frac{W_r}{W_m} = \frac{\frac{2}{3}\frac{Q^2v^2}{c^2\delta}}{\frac{1}{3}\frac{Q^2v^2}{ac^2}} \tag{37}$$

$$= \frac{2a}{\delta} \tag{38}$$

Thus, in the case of a charge in motion being brought to rest, the fraction of the energy radiated is inversely proportional to the thickness δ of the resulting pulse, which, in turn, is proportional to the time required to stop the charge.

Second, to determine the energy radiated per vibration by a charge which, having been set into vibration by some disturbance, is executing simple harmonic vibrations about an equi-

librium position: Such a charge will gradually be brought to rest by virtue of the energy radiated on account of the acceleration which the charge experiences at various parts of its path. At time t let the displacement x of the charge Q from its position of equilibrium be given by the usual equation of simple harmonic motion

$$x = A \sin 2\pi\nu t \tag{39}$$

where A is the amplitude of the vibration and ν is the frequency. Differentiating to obtain the velocity v and the acceleration g of the charge gives

$$v = \frac{dx}{dt} = 2\pi\nu A \cos 2\pi\nu t \tag{40}$$

$$g = \frac{d^2x}{dt^2} = -4\pi^2\nu^2 A \sin 2\pi\nu t \tag{41}$$

From equation (36), we have, for the quantity of energy dW radiated in time dt,

$$dW = \frac{2}{3}\frac{Q^2g^2}{c^3}\,dt \tag{42}$$

$$\therefore dW = \frac{2}{3}\frac{Q^2}{c^3}(-4\pi^2\nu^2 A \sin 2\pi\nu t)^2 dt$$

$$= \frac{32\pi^4}{3}\frac{Q^2}{c^3}\nu^4 A^2 (\sin^2 2\pi\nu t)dt \tag{43}$$

To obtain the energy W_1 radiated during a complete vibration, we must integrate this equation over an entire period, *i.e.*, from $t = 0$ to $t = 1/\nu$. That is,

$$W_1 = \frac{32\pi^4}{3}\frac{Q^2}{c^3}\nu^4 A^2 \int_{t=0}^{t=\frac{1}{\nu}} (\sin^2 2\pi\nu t)dt$$

The value of the integral is $\frac{1}{2\nu}$.[1] Therefore,

$$W_1 = \frac{16\pi^4}{3}\cdot\frac{\nu^3}{c^3}Q^2A^2 \tag{44}$$

The absolute value of W_1 is not so important as the ratio p_1 which W_1 bears to the total energy of the vibrating system, for it is this ratio which determines the number of waves in the electromagnetic wave train which the vibrating charge will

[1] $\int \sin^2\phi d\phi = \phi/2 - \frac{1}{4}\sin 2\phi$. To integrate, let $\phi = 2\pi\nu t$. Then dt becomes $\frac{d\phi}{2\pi\nu}$ and the limits become 0 and 2π, respectively.

emit before it is brought to rest by the "damping" due to the process of radiation. The total energy of the vibrating system is given by

$$W_0 = \tfrac{1}{2} m v_m^2 \tag{45}$$

where m is the (electromagnetic) mass of the charge (m is given by equation (22)) and v_m is the maximum velocity, *i.e.*, the velocity at midpoint of the path. From equation (40), v_m^2 is given by

$$v_m^2 = 4\pi^2 \nu^2 A^2 \tag{46}$$

Therefore,

$$p_1 = \frac{W_1}{W_0} = \frac{8\pi^2}{3} \cdot \frac{Q^2}{mc^3} \nu \tag{47}$$

This equation shows that the fraction p_1 is proportional to the frequency ν of the vibration. That is, longer wave trains will be emitted when the frequency of vibration is low than when it is high.

An alternative, and rather suggestive, expression for the ratio p_1 is obtained by introducing into equation (47) the value of m from equation (22). We, then, have

$$\begin{aligned} p_1 &= 4\pi^2 a \frac{\nu}{c} \\ &= 4\pi^2 \frac{a}{\lambda} \end{aligned} \tag{48}$$

where λ is the wave length of the radiation emitted by the vibrating charge and a is the "diameter" of the charge.

In subsequent chapters, we shall consider the application of some of the important formulæ derived in this chapter.

CHAPTER VI

THE PHOTOELECTRIC EFFECT

An approach to that outstanding problem of modern physics, namely, the nature of radiant energy, is most directly made by a study of the *experimental facts* of the photoelectric effect. In its broadest meaning, the term "photoelectric effect" might be used to include several phenomena, more or less related, which involve the interaction between light and electricity, such as the change in resistance of selenium when illuminated by red or near infra-red light; the change in e.m.f., when illuminated, of certain cells containing fluorescent materials, as electrolytes; or, indeed, the rotation of the plane of polarization of a beam of light when passing through a medium placed in a strong electric field. In the broad use of the term, even dispersion is a photoelectric phenomenon, since it involves a reaction between light and the electrical charges in matter. That such interactions should take place is not surprising if light be an *electro*magnetic phenomena and if matter be made up of, or contain, charged particles. In this chapter, we shall restrict the use of the term "photoelectric effect" to the discharge of negative electricity from bodies when illuminated by light of appropriate wave length. We shall make no attempt to give a complete outline[1] of this interesting subject. Rather we shall discuss photoelectricity only in so far as may be necessary to point out the embarrassing situation in which the electromagnetic theory of light finds itself in attempting to account for the phenomena observed.

1. The Discovery by Hertz.—Reference has already been made (p. 111) to the experiments of Hertz in which he demonstrated the existence of the electromagnetic waves predicted by Maxwell. In these experiments, Hertz was using two spark gaps, which we may represent diagrammatically by P and S (Fig. 27). The terminals of P were suitably connected to an induction coil, and the spark discharge across P was oscillatory,

[1] The reader is referred to ALLEN, H. STANLEY: "Photoelectricity" 2d ed. (1925).

giving rise to electromagnetic waves. These waves were "detected" by a suitably tuned circuit containing the spark gap S, the length of which could be adjusted by a micrometer. The maximum length of S which would give continuous sparking was taken as a measure of the strength of the "signal" received by the secondary. But Hertz observed that this critical length of the spark gap S seemed to be determined not only by the strength of the signal but also by other factors as well. For example, when, to facilitate observation, he enclosed S in a black box, say of cardboard, *the critical length of S was much less.*

This disturbing factor might have escaped further study in the hands of a less observant investigator. But Hertz essayed to discover its cause. He observed that the interposition between P and S of any opaque object, such as a piece of board or black paper, was just as effective in reducing the critical length of S as if S were completely surrounded by the box. Further tests showed that a piece of glass interposed between P and S acted as an opaque screen. A plate of quartz, however, produced no effect. Since glass is opaque to ultra-violet light, while quartz is transparent, and since the primary spark P produced ultra-violet light, Hertz concluded that the increase in the critical length of S when not shielded from P was due to the ultra-violet light from the primary spark gap P falling on the secondary gap S. He tested this conclusion in various ways, for example by screening S from P and allowing ultra-violet light from another source to fall on S. And he found that the light must fall on the *terminals* themselves, not simply in the space between. Illuminating the negative terminal was most effective. Further, the terminals must be "clean and smooth." Recognizing the importance of the discovery, Hertz published his results[1] in a paper entitled "An Effect of Ultra-violet Light upon the Electric Discharge" and then returned to his investigation of electromagnetic waves.

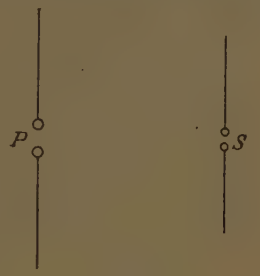

FIG. 27.

2. Some Early Experiments.—The extraordinary importance of Hertz's discovery at once attracted numerous investigators.

[1] *Ann. Physik*, vol. 31, p. 983 (July, 1887). See, also, the English translation of HERTZ's "Electric Waves."

A very fundamental result was soon announced by Hallwachs,[1] who found that a freshly polished zinc plate, insulated and connected to an electroscope as an indicator, would, when charged *negatively* and illuminated by ultra-violet light from an arc lamp, lose its charge, but that there was no effect if the charge was *positive*.[2] Aluminum was found more active than zinc; iron, less so. Hallwachs concluded that, in some mysterious manner, when the plate was negatively charged and illuminated, negatively electrified particles were emitted from the plate. He even observed, by using an electrometer instead of an electroscope, that a *neutral* insulated plate, when illuminated, would acquire a small *positive* potential, *i.e.*, in present-day terminology, would lose a *negative* charge. In other words, not only did light *permit the escape* of negative electricity from a negatively electrified plate: it even *caused the expulsion of negative electricity from a neutral plate.*

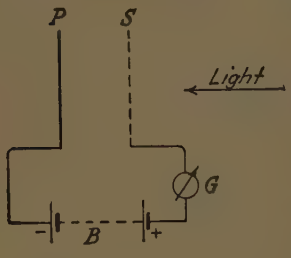

FIG. 28.

Stoletow[3] devised an arrangement, shown diagrammatically in Fig. 28, for producing a continuous *photoelectric current.* P is a photoelectrically sensitive plate, say a polished zinc plate, connected to the negative terminal of a battery B of several cells. S is a wire grating or gauze connected to the positive terminal of the battery through a very sensitive galvanometer, or an electrometer G. When ultra-violet light falls upon P, *a continuous current is observed in* G, indicating that a negative charge is flowing from P to S. No current flows if the battery be reversed. P corresponds to the cathode in an electrolytic cell, and S to the anode.

Elster and Geitel[4] showed that there is a close relation between the contact potential series of metals and the photoelectric

[1] *Ann. Physik*, vol. 33, p. 301 (January, 1888).

[2] This experiment is very easily performed. Take a piece of zinc, scratch one side with sandpaper so as to expose a fresh surface, suspend it by a wire or string from an ebonite rod or other good insulating support and connect the plate to an ordinary electroscope. An ordinary (carbon) arc lamp is a suitable source of ultra-violet. The difference between the polished and the unpolished side is at once observable, as is also the effect of glass, quartz plates, etc., between source and plate.

[3] *Jour. phys.*, vol. 9, p. 486 (1890).

[4] *Ann. Physik*, vol. 38, pp. 40 and 497 (1889).

effect. The more electropositive the metal the longer the wave length to which it would respond photoelectrically. The alkali metals, sodium, potassium, and rubidium, were sensitive even to light of the visible spectrum.

It was early observed[1] that the photoelectric effect took place even in the highest attainable vacuum. For example, if the plates P and S, in Fig. 28, be enclosed in a glass bulb fitted with a quartz window for admitting ultra-violet light, the photoelectric current is observed to flow even if the bulb be evacuated as thoroughly as possible. This shows that the gas surrounding the plate plays no essential role in the photoelectric effect.

3. A Problem.—An important question now arises. What is the mechanism by which negative electricity is transferred from the cathode P to the anode S, Fig. 28? That the charge is carried by negatively electrified particles was suggested by the experiments of Elster and Geitel,[2] who showed that a transverse magnetic field diminishes the photoelectric current if the phenomenon takes place in a vacuum. But what are the particles?

Negative answers to this question were readily obtained. The fact that the effect persisted even to the highest attainable vacuum and was quite independent of the "degree" of the vacuum after a certain low pressure had been reached seemed to indicate that the gas molecules themselves in the region between P and S could not act as carriers of the charge.

The suggestion was made that, perhaps, under the influence of light, particles of the cathode became detached, and since they would naturally be charged negatively, they might move under the influence of the electric field from cathode to anode. This suggestion was made untenable by an experiment by P. Lenard,[3] in which a clean platinum wire acted as anode, and a sodium amalgam as cathode, both being in an atmosphere of hydrogen. The photoelectric current was allowed to flow until about 3×10^{-6} coulombs had passed through the circuit. If the carriers of the charge be atoms of sodium, each atom could hardly be expected to carry a larger charge than it carries in electrolysis. Taking the electrochemical equivalent of sodium as 0.00024 grams per coulomb, there should have been deposited on the

[1] RIGHI, *Mem. Acad. di Bologna*, vol. 9, p. 369 (1888); STOLETOW, *Jour. phys.*, vol. 9, p. 468 (1890). LENARD, P., *Ann. Physik.*, vol. 2, p. 359 (1900).

[2] *Ann. Physik*, vol. 41, p. 161 (1890).

[3] *Ann. Physik*, vol. 2, p. 359 (1900).

platinum wire at least 0.7×10^{-6} milligrams of sodium, a quantity sufficient to be detectable by the well-known flame test.[1] On removing the wire from the bulb, no trace of sodium could be detected. Evidently, particles (molecules) of the cathode did *not* act as carriers of the photoelectric current.

If the photoelectric current was carried neither by molecules of the gas surrounding the cathode nor by molecules of the cathode itself, what *were* the carriers? The answer to this question came as a result of the convergence of a number of different lines of evidence which finally culminated in the discovery of the electron by J. J. Thomson and in direct experimental proof of the electrical nature of matter. We shall interrupt the discussion of the photoelectric effect proper to consider briefly some of these developments.

4. The Laws of Electrolysis.—The laws of electrolysis discovered by Faraday suggested that associated with each univalent ion was an elementary charge e which was the same for all ions. This is readily seen. Faraday's two laws may be stated

$$M = k \cdot i \cdot t = kQ \tag{1}$$

$$k = h \frac{A}{V} \tag{2}$$

where M is the mass, in grams, of one type of ion (say Cu^+ in the electrolysis of $CuSO_4$) deposited by a current i flowing for t seconds; k is the electrochemical equivalent of the ion; A is the atomic weight; and V the valency of the ion in the compound; h is a proportionality constant which is numerically equal to the electrochemical equivalent of hydrogen for which, in equation (2), A and V are both unity.[2] Also, by definition, $Q = i \cdot t$. Combining equations (1) and (2), we may solve for Q:

$$Q = \frac{1}{h} \cdot \frac{M}{A} \cdot V \tag{3}$$

A gram-atom of any element is a quantity of the element, the mass of which M_A in grams is numerically equal to the atomic weight. That is,

$$M_A = A$$

for a gram-atom. Thus, a gram-atom of Na is 23.00 grams of Na; of Cl, 35.46 grams; of Cu, 63.57 grams; etc. When Na and

[1] Bunsen had shown that 0.3×10^{-6} mg. of sodium could easily be detected in the flame.

[2] A for hydrogen is really 1.0077.

Cl unite, atom for atom, to form NaCl, 23.00 grams of Na combine with 35.46 grams of Cl. That is, 23.00 *grams of Na contain the same number of atoms as* 35.46 *grams of Cl.* Similarly, 1 gram of hydrogen contains the same number of atoms as 35.46 grams of chlorine. This number of atoms N in a gram-atom of any element is the same for all elements and is called *Avogadro's number;* it is one of the fundamentally important constants in chemistry and physics. We shall discuss its numerical value later.

Similarly, if we define a gram-molecule, or a mole, as a quantity of the substance the mass of which in grams is numerically equivalent to the molecular weight (*e.g.*, 159.63 grams[1] of $CuSO_4$); or a gram-ion as a quantity of the ion the mass of which is numerically equal to the "ionic" weight (*e.g.*, 96.06 grams of SO_4), it is obvious that the number of molecules in a gram-molecule, or of ions in a gram-ion, is, also, N.

If, by electrolysis, we free a gram-atom, M_A, of a univalent element, equation (3) shows that the quantity of electricity Q_A required is given by

$$Q_A = \frac{1}{h} \qquad (4)$$

since, then, $M_A = A$ and $V = 1$. This quantity Q_A is, thus, seen to be the same for all univalent atoms and is a universal constant. It is called the "faraday." Its numerical value is readily obtained by taking the reciprocal of the electrochemical equivalent h of hydrogen.[2] According to the best modern determinations,

$$Q_A = 9{,}650 \text{ electromagnetic units}$$

But a gram-atom of *any* element contains N atoms; and to free these N (univalent) atoms, in electrolysis, requires Q_A units of electricity, *whatever the element.* The charge e carried by each atom (we should, more correctly, say "ion") is, therefore, obviously,

$$e = \frac{Q_A}{N} \qquad (5)$$

[1] Taking atomic weights, *viz.:* Cu, 63.57; S, 32.06; O, 16. These are more correctly called "combining weights." In any event, they do not give the relative weights of *atoms* of the several elements. There is no atom of chlorine, for example, which has a relative weight (mass) of 35.46, taking oxygen 16. Rather, chlorine has two kinds of atoms: one group with a relative mass of 35 and the other with a relative mass of 37; and these two kinds of chlorine atoms (isotopes of chlorine) are mixed in the approximate proportion of 3 of the former to 1 of the latter (see Chap. XIII).

[2] See Note[2], preceding page.

and is the same for all *univalent* ions. The value of Q_A was early determined. Had N been known, the value of the elementary charge e could, also, have been determined. As a matter of fact, we shall see, later, that the best method of determining N, the number of atoms in a gram-atom, is by dividing Q_A by the independently determined value of e.

Although the facts of electrolysis do not give a means of determining e, they do give a method of determining the ratio of the charge e to the mass m of the atom or ion. For, the mass of an atom is given by[1]

$$m = \frac{A}{N} \tag{6}$$

where A, as before, is the atomic weight.
And accordingly,

$$\frac{e}{m} = \frac{Q_A/N}{A/N} = \frac{Q_A}{A} \tag{7}$$

That is, the ratio of the charge e carried by an ion to the mass m of the ion is obtained by dividing the faraday Q_A by the atomic weight A. Since Q_A is constant, the ratio e/m is inversely proportional to the atomic weight A. The maximum possible value of e/m for univalent ions in electrolysis is that for hydrogen for which, since A for hydrogen is unity, $\left(\frac{e}{m}\right)_H = 9650$. Thus, the facts of electrolysis gave fairly direct experimental evidence of the association with each atom or ion of an elementary charge e (or a charge $2e$ with a divalent ion), *but they afforded no means of determining the value of e.*

Computations based on the kinetic theory of gases, however, indicated that N is, at least, of the order of 10^{23}. Consequently, by equation (4), e was known to be of the order of 10^{-20} e.m.u., or 10^{-10} e.s.u.

5. Dispersion of Light.—We have seen, in Chap. IV, that the failure of the early form of the electromagnetic theory of light to predict the phenomenon of dispersion led to the introduction of the concept, first developed by L. Lorenz,[2] of the existence in refractive media of charges, or charged bodies, with a charge e and mass m which, when disturbed, could vibrate with a natural period ν_0 about a fixed, equilbrium position. The extension of

[1] Since A grams of the element contain N atoms.
[2] *Ann. Physik*, vol. 11, p. 70 (1880).

this theory by H. A. Lorentz[1] and others, and the success with which the resulting formulæ explained the observed facts of dispersion, both normal and anomalous, gave great weight to the concept of the electrical constitution of matter.

6. The Zeeman Effect.—In 1862, Faraday, looking for a possible effect of a magnetic field upon a light source, placed a sodium flame between the poles of a strong electromagnet and examined the D lines by a spectroscope. He was unable to detect any change in the appearance of the lines by turning on the magnetic field.

Faraday's failure to observe the effect which he expected was due to the inadequate resolving power of his apparatus. For, in 1896, Zeeman,[2] repeating Faraday's experiment, with the improved technique then available, discovered that spectral lines are split up into components when the source emitting the lines is placed in a very strong magnetic field and, further, that these components are polarized. The simplest case is shown in Fig. 29, where a represents a line before the magnetic field is turned on. If the field be turned on and the line be viewed *at right angles* (R) to the direction of the field, the line is seen to be triple with components l_R, a', and r_R. The central line a' has the same wave length as the original line a but is plane polarized in a plane *at right angles* to the magnetic field H, the direction of polarization being indicated by the double arrow above the line. The other two components l_R (left, shorter wave length) and r_R (right, longer wave length) are plane polarized in a direction *parallel* to the magnetic field.

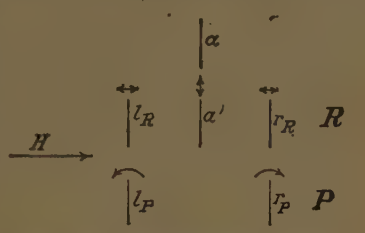

FIG. 29.—Diagrammatic representation of the Zeeman effect: a is the original line; R shows the three components when viewed at right angles to the magnetic field; P shows the two components when viewed parallel to the field.

If the pole pieces of the electromagnet be drilled through longitudinally so that one may view the flame in a direction parallel to the magnetic field, only two components l_P and r_P are seen, as shown at P. These two lines have the same respective wave lengths as the outside components in the previous case, but they are *circularly* polarized in opposite directions, as shown

[1] LORENTZ, H. A.: "The Theory of Electrons" (1909).
[2] *Phil. Mag.*, vol. 43, p. 226 (1897).

by the arrows above the lines. (The magnetic field, in this latter case, is directed toward the reader.)

In his original paper announcing his discovery, Zeeman offered a relatively simple, yet at that time adequate, explanation of the phenomenon on the basis of Lorentz' electrical theory of matter mentioned in the preceding section. Let it be assumed that light waves originate in the vibratory motion of electric charges associated with atoms, and consider the effect of a magnetic field on such vibrations. In Fig. 30, let O represent the normal position of equilibrium, within an atom, of a particle which has a charge[1] e' and a mass m. When the particle is displaced, in any direction, by an amount x from O, let the return force f be given by

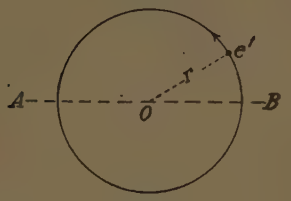

FIG. 30.

$$f = -px \tag{8}$$

where p is a constant. When so disturbed, the particle will vibrate about its position of equilbrium with a period T, given by

$$p = \frac{4\pi^2 m}{T^2} \tag{9}$$

according to the ordinary laws of simple harmonic motion. Or, if the particle be set in motion in a circular path of radius r about point O as a center, the motion will be governed by the equation

$$\frac{mv^2}{r} = pr \tag{10}$$

Let ω_o be the angular velocity about O. Then $v = \omega_o r$, and, by equations (9) and (10),

$$\omega_0^2 = \frac{p}{m} = \frac{4\pi^2}{T_0^2} \tag{11}$$

Now, let a magnetic field of strength H be applied at right angles to the plane of the paper (Fig. 30) and directed away from the reader. The charge, in its orbital motion, will experience an additional force f_H, due to its velocity v (at right angles to the field H), which, according to equation (14), Chap. V, will be

$$f_H = He'v \tag{12}$$

[1] The prime (′) denotes that e is in electromagnetic units.

If the charge be positive, and the motion counterclockwise, as shown, f_H will be in the same direction as f, *i.e.*, toward O, and we may write, instead of equation (10),

$$\frac{mv^2}{r} = pr + He'v \tag{13}$$

Putting $v = \omega_1 r$, where ω_1, is the angular velocity after the field is applied, we have, after rearranging,

$$\omega_1^2 - H\frac{e'}{m}\omega_1 = \omega_0^2 \tag{14}$$

since, by equation (11), $p/m = \omega_0^2$. Completing the square on the left-hand side of equation (14) and extracting the square root gives

$$\omega_1 - \frac{He'}{2m} = \sqrt{\omega_0^2 + \frac{H^2e'^2}{4m^2}} \tag{15}$$

Or, since, as we shall show later, we may neglect the second term under the radical in equation (15) in comparison with ω_0^2, we have

$$\omega_1 = \omega_0 + \frac{He'}{2m} \tag{16}$$

If we had considered a clockwise motion instead of a counterclockwise one, we should have obtained

$$\omega_2 = \omega_0 - \frac{He'}{2m} \tag{17}$$

Changing angular velocities to frequencies of revolution by writing $\omega_0 = 2\pi\nu_0$, $\omega_1 = 2\pi\nu_1$ and $\omega_2 = 2\pi\nu_2$, we have, instead of equations (16) and (17),

$$\nu_1 = \nu_0 + \frac{He'}{4\pi m} \tag{18a}$$

$$\nu_2 = \nu_0 - \frac{He'}{4\pi m} \tag{18b}$$

Equations (18) show that the frequency of the radiation emitted by the charge in orbital motion in the magnetic field, as in Fig. 30, will be either greater, ν_1, or less, ν_2, than the frequency ν_0 emitted when the field is absent, according as the motion is counterclockwise or clockwise; and, further, that this difference is proportional to the field strength H.

It can be shown that these principles are equally applicable to the case of a *linear* vibratory motion, as, for example, a motion over the path AOB (Fig. 30). For, we may regard a linear simple harmonic vibration as made up of two equal and oppositely

directed circular motions, each of which, under the influence of the magnetic field, will behave as specified by equations (18), the counterclockwise component moving with greater angular velocity than the clockwise. The effect of this is to cause the path AOB to rotate, slowly, counterclockwise about O. Indeed, this is exactly what would happen to the path of a charge set vibrating at right angles to a magnetic field. In Fig. 31, let the magnetic field be, as before, perpendicular to the plane of the paper and directed away from the reader. A positive charge moving from A_1 toward B_1 will experience a force, at right angles to its motion, which will deflect it upward toward B_2.

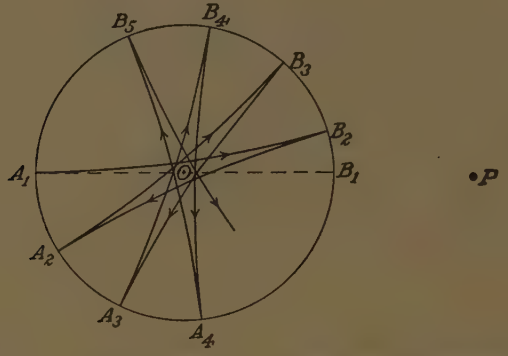

FIG. 31.—Effect of a magnetic field on a charged body vibrating initially with simple harmonic motion at right angles to the field.

On the return path, the direction of the force due to the magnetic field is reversed, and the path bends downward toward A_2, etc. Thus, the path rotates slowly about O. When the path is in the general direction A_1B_1, the intensity of the radiation sent out toward point P is a minimum;[1] while, when the path coincides with A_4B_4, the radiation toward P is a maximum. An observer at P would receive from the vibrating charge a radiation of periodically varying intensity—which is exactly what would be observed if the source of radiation were *two* vibrating systems of slightly different period, their effects at P being alternately in phase and out of phase. A spectroscope, receiving this radiation, should resolve it into two components of slightly different frequency. We are, therefore, justified (1) in regarding the (linear) vibratory motion as made up of two oppositely directed

[1] The apparent amplitude, as seen from the direction of P, is then small.

circular motions, which, under the influence of the magnetic field, revolve with slightly different frequencies and (2) in applying to such a vibratory system equations (18).

The observations recorded diagrammatically in Fig. 29 may be readily explained on the basis of the above principles. Assuming that light waves are the electromagnetic waves emitted by electric charges vibrating with simple harmonic motion about fixed equilibrium positions within the several atoms of the light source, let O (Fig. 32) be the light source which is placed in a magnetic field of strength H, the direction of the field coinciding with the x-axis. We may resolve the vibrations of the charges into components parallel to each of the three axes, respectively. Vibrations parallel to Ox will not be affected by the presence of the field and will send out toward z radiation of the same frequency ν_0, as if there were no field. This accounts for the presence of the "undeviated" line a', of Fig. 29, R. But this same vibration will emit *no* radiation in the direction Ox, since, to an observer looking from x toward O, the vibrating charge will seem to stand still. This explains the absence of the undeviated component in Fig. 29, P. Components of vibrations at right angles to Ox will behave exactly as illustrated in Fig. 31, and there will be emitted in the direction Oz, as well as in the direction Ox, radiations whose frequencies differ from ν_0 by the amount $\pm \frac{He'}{4\pi m}$, as given by equations (18). This accounts for the lines l_R, r_R, l_P, and r_P, in Fig. 29.

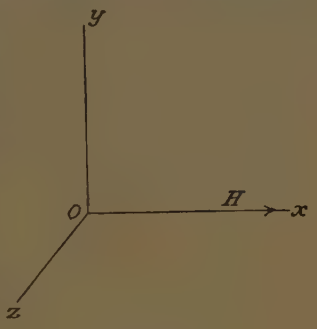

FIG. 32.

If $\Delta\nu$ represents the difference in frequency between the original line and any one of the shifted components, we have

$$\Delta\nu = \frac{He'}{4\pi m}$$
$$\therefore \frac{e'}{m} = \frac{4\pi}{H}\Delta\nu \qquad (19)$$

By measuring $\Delta\nu$ and the corresponding value of H, it is possible to compute the ratio e'/m, that is, the ratio of the charge e' of the vibrating particles to the mass m of the particles. In this way,

Zeeman, in his first paper (March, 1897), determined[1] that "e'/m is of the order of magnitude of 10^7 electromagnetic units."

In a later experiment,[2] working with much higher resolving power, Zeeman found a value of e'/m of 1.6×10^7. In this experiment, he used a magnetic field of 22,400 gauss, which caused a wave-length change, in the case of the D lines of sodium, of about 1 part in 18,000.

The Zeeman effect and its explanation seemed to give final confirmation of the electromagnetic origin of light and to adduce some evidence as to the nature of the charged particles which take part in the process, for the value of e'/m determined in this way is in substantial agreement with the value determined by J. J. Thomson for cathode particles by a method which will be described in the next section.

7. The Discovery of the Electron by Sir J. J. Thomson.—(*a*) Previous to 1897, many studies had been made of that beauti-

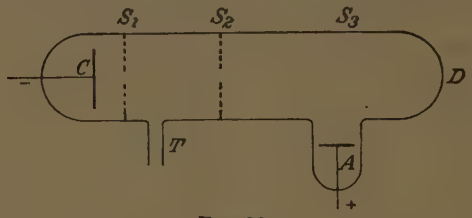

FIG. 33.

ful phenomenon, the discharge of electricity through rarified gases. Diagrammatically, let the discharge from an induction coil or an electrostatic machine pass between the negative terminal C (cathode) and the positive terminal A (anode), sealed into a glass tube (Fig. 33), which is being exhausted through the side tube T. At atmospheric pressure, the discharge, if the potential be high enough, is a spark between the terminals. As the evacuation proceeds, this spark widens out into a glow which fills the whole tube; then striations appear, which, as the pressure gets lower, recede toward A. At a very low pressure, there appears around the cathode a dark space, known as the "Crookes' dark space," which, with further decrease in pressure, grows longer (*i.e.*, extends farther toward A), until, finally, the edge of the dark space reaches the glass walls of the tube. The glass is then

[1] Zeeman's first apparatus was not of sufficient resolving power to separate the components. He observed a widening of the line on turning on the field.

[2] *Phil. Mag.*, vol. 44, p. 255 (September, 1897).

observed to glow with a color (greenish or bluish), depending on the kind of glass of which the tube is made. This "something" which seems to proceed from the cathode and causes the phosphorescence of the glass was early called "cathode rays."

There was much controversy as to the nature of these "rays." The German school of physicists held the opinion that the rays were due to some process in the ether; while the English physicists believed that the rays consisted of particles, charged with negative electricity and shot off at high velocity from the cathode. In support of the latter view were experimental facts such as the following:

1. *The rays are deflected by a magnetic field.* If the cathode rays be restricted to a narrow pencil by screens S_1 and S_2 (Fig. 33), a small phosphorescent spot is observed on the glass wall at D. If the tube be then subjected to a magnetic field the direction of which is at right angles to the plane of the paper and directed away from the reader, the spot D moves *downward*—which is exactly what would take place if the rays consisted of *negatively* charged particles moving *from C toward A*.
2. *The rays are deflected by an electrostatic field.* With screens S_1 and S_2 in place, as shown, an *electrostatic* field parallel to the plane of the paper (and at right angles to the direction CD) will deflect the spot D either upward or downward, according as the *positive* direction of the field is downward or upward.
3. If S_1 and S_2 be removed, the entire end of the tube at D will glow. But a small, solid obstacle, placed at S_3 and partly filling the tube, will cast a shadow at D, indicating that "something" is proceeding *from C toward D*.
4. *The rays exert mechanical effects.* (*a*) If the cathode be suitably curved, the rays may be "focused" at some point within the tube. A piece of platinum foil placed at this focus may, if the rays be sufficiently intense, be heated to incandescence. (*b*) A "paddle" wheel, mounted on suitable guides, may be made to revolve by making the rays strike the paddles.
5. *The rays transport negative electricity.* This was shown by Perrin,[1] by allowing the rays to enter an insulated chamber connected to an electroscope.

[1] *Compt. rend.*, vol. 121, p. 1130 (1895).

Final confirmation of the correctness of the view that cathode rays are moving negatively charged particles came from the classical experiments[1] of J. J. Thomson, whose *quantitative* determination of the ratio of the charge e' of the particles to their mass m carried more weight than did the *qualitative* evidence mentioned in the preceding paragraph.

(*b*) Thomson's experiments are so fundamental in the history of the electrical theory of matter as to warrant description. The highly evacuated glass tube (Fig. 34(*a*)), contains the cathode C and an anode A, which has a small rectangular slot in it through which the cathode rays may pass. B is a screen similar

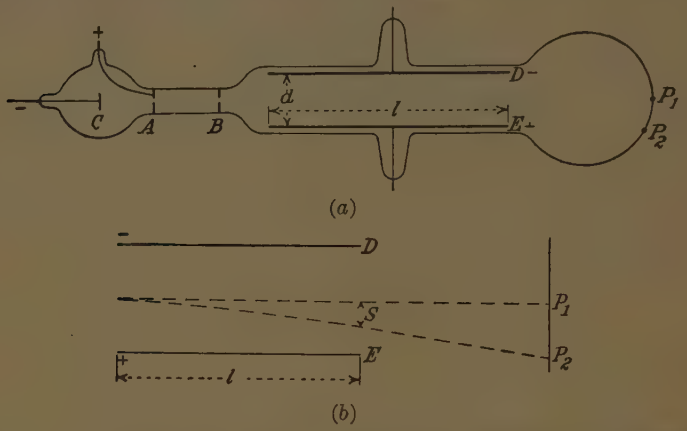

FIG. 34.—(*a*) Thomson's apparatus for determining the ratio e/m for electrons; (*b*) Deflection of an electron by the electrostatic field in Thomson's apparatus.

to, and electrically connected with, A. Cathode rays, accelerated from C toward A, after passing the slot in A move with uniform velocity and emerge from the slot in B as a small bundle of rectangular cross-section, which, on reaching the far side of the bulb, causes a small, phosphorescent patch at some such point as P_1. But when a potential difference V is maintained between the parallel plates D and E, E being positive, the spot appears at P_2, having been deflected downward by the electrostatic field. A pair of Helmholtz coils, not shown, whose diameters are equal to the length of the plates D and E are placed, one in front and the other behind the tube, so as to produce a magnetic field, perpendicular to the plane of the paper, the strength of which can be determined from the dimensions of the coils and the

[1] *Phil. Mag.*, vol. 44, p. 293 (October, 1897).

current through them. If the magnetic field is directed *toward* the reader, the spot P_1 will be deflected *upward*.

Two experiments are now performed:

1. With a given electrostatic field between the plates deflecting the spot downward, the strength of the magnetic field deflecting the spot upward again is adjusted to such a value as will cause the spot to return to the original undeviated position P_1.
2. The magnetic field is removed and the deflection P_1P_2 caused by the electrostatic field alone is measured.

From these two experiments, the ratio e'/m may be determined as follows:

Let e' = charge of moving particle (in e.m.u.).
m = mass of particle.
d = distance between plates D and E.
l = length of plates.
V = potential difference (in e.m.u.) applied between D and E.
$F = V/d$ = electric field between plates.
H = magnetic field.
v = the (horizontal) velocity[1] with which particles emerge from B.

In experiment 1, the downward force f_F, produced by the electrostatic field and given by

$$f_F = F \cdot e' \tag{20}$$

is just equal and opposite to the upward force f_H, due to the magnetic field and given by

$$f_H = He'v \tag{21}$$

Therefore,

$$He'v = Fe'$$

or,

$$v = \frac{F}{H} \tag{22}$$

Experiment 1, therefore, gives a means of measuring the (horizontal) velocity with which the particles pass between the plates. This velocity is determined, of course, by the potential

[1] This horizontal velocity is constant over the entire path B to P_1 since there are no horizontal forces acting on the particle.

difference applied between C and A and, to a certain extent, by the vacuum.

From the second experiment, it is possible to determine the downward deflection which the particles experience in passing *between* the plates. Let this deflection be S (Fig 34(*b*)). The downward force experienced by the particle while passing between the plates is given by equation (20), and the downward *acceleration* a is given by

$$a = \frac{Fe'}{m}$$

This downward acceleration is constant over the length of path l. If t is the time required to pass over this path, then, by the ordinary laws of uniformly accelerated motion,

$$S = \frac{1}{2} F \frac{e'}{m} t^2 \qquad (23)$$

where $t = l/v$. All quantities in this equation are known except e'/m, which may, therefore, be computed.

Thomson found that the value of e'/m determined in this way was of the order of 10^7 and that *it was independent of the kind of gas in the tube* (air, H_2, or CO_2) and, likewise, independent of the material of the electrodes (Al, Fe, or Pt). A later determination gave

$$\frac{e'}{m} = 1.7 \times 10^7 \qquad (24)$$

a value numerically identical (almost) *with the value of* e'/m *determined from the Zeeman effect for the particles taking part in light emission, which particles, therefore, seemed to be identical with cathode rays.*

(*c*) This value of e'/m is very much larger (seventeen hundred times) than the value of e'/m for hydrogen atoms in electrolysis, as discussed on page 142. This large value of e'/m might result either from a large value of e' or a small value of m, or both. It became a matter of much importance to determine the charge e' carried by these particles.

The charge e' was measured by H. A. Wilson, by a method based on the following principles: When a gas, saturated with water vapor, is cooled by expansion, condensation into droplets tends to take place around any dust particles present. Similar condensation will take place if the gas contains positive or negative ions—such as are produced by the passage of X-rays or

gamma rays of radium through the gas—condensation taking place more easily around the negative ions than around the positive. By suitably regulating the expansion, it is possible to get a "cloud" of small, negatively charged droplets. The mass M of a given droplet can be determined by observing, with a microscope, the velocity v, with which the droplet slowly falls under the action of gravity, v depending on the viscosity η of the air, the radius a of the drop, and the acceleration due to gravity g, according to the (approximate) equation

$$v = \frac{2}{9}\frac{g}{\eta}a^2 \tag{25}$$

Observing v, and knowing g and η, a may be determined, from which

$$M = \tfrac{4}{3}\pi a^3 \rho \tag{26}$$

where ρ is the density of water, assumed unity. The downward force due to gravity, Mg, may now be balanced by an electric field F causing an upward force $F \cdot e'$, so that

$$Mg = Fe',$$

from which e' may be determined. The value of e' was found, in this way, to be of the order of 1×10^{-20} electromagnetic units, or 3×10^{-10} electrostatic units, in substantial agreement with the approximate value of the charge carried by a univalent ion in electrolysis, as discussed in Sec. 4 of this chapter.

Clearly, the large value of e'/m for cathode particles, cited in equation (24), is due to a very small value of m rather than to a large value of e. Assuming, as is seen to be approximately justified, that the charge carried by the cathode particle is the same as that carried by the hydrogen atom in electrolysis, it follows that *the mass of the cathode particles must be of the order of* 1/1,700 *of the mass of the hydrogen atom, which* up to the time of Thomson's experiments, *was the smallest known particle.*

(*d*) Here, then, in the cathode stream, we are dealing with previously unknown particles, of very small mass and carrying a negative charge, which Thomson referred to as "corpuscles," or "primordial atoms," but which have since become known as *electrons*, and which are now regarded as one of the two primordial substances out of which all matter is composed. Since its discovery by Thomson, in 1897, the electron has played such an everyday part in modern physics that a detailed discussion of

it need not be undertaken here. According to the most recent data,[1] the values of e, m and e/m for the electron are

$$e' = 1.592 \times 10^{-20} \text{ e.m.u.}$$
$$e = 4.774 \times 10^{-10} \text{ e.s.u.}$$
$$\frac{e'}{m} = 1.769 \times 10^{7} \text{ e.m.u. per gram}$$
$$\frac{e}{m} = 5.305 \times 10^{17} \text{ e.s.u. per gram}$$
$$m = 8.999 \times 10^{-28} \text{ grams}$$

The discovery of the electron by Thomson and the recognition of the fact that it is one of the constituent parts of all atoms made possible the explanation of a number of more or less diverse phenomena on the basis of a single concept. Thus, the electrical nature of matter was, at once, made apparent. Since atoms in the normal state are observed to be electrically neutral, if they contain negatively charged electrons, they must, also, contain positive electricity in some form. The phenomenon of electric conduction in metals was ascribed to the existence, in the interatomic spaces of the metal, of "free" electrons, which, drifting under the influence of an applied electric field (*i.e.*, the potential difference at the terminals of the conductor), caused the transport of charge, the actual direction of motion of the electrons being opposite to the convention concerning the *positive* direction of current. The variation of electrical resistance with temperature also received a ready explanation. The fact that the ratio e/m for electrons was observed to be the same as the ratio of e/m for the vibrating particles in the Zeeman effect lead directly to a confirmation of the previously made assumption that *light*

[1] International Critical Tables, vol. I, p. 12. Mention should be made of the fact that in the literature of physics the charge on the electron is most frequently expressed in *electrostatic* units, while the ratio of charge to mass is usually given in *electromagnetic* units per gram. This usage has an historical basis only.

For a fuller account of the determination of the electronic charge e the reader is referred to MILLIKAN'S "The Electron." The accurate measurement by Millikan of the electronic charge e, although by a method substantially the same in principle as Wilson's method described above, is one of the outstanding investigations in modern physics, not only because of the fundamental importance of the quantity measured, but also because of the very skillful way in which the many experimental difficulties were overcome.

waves originate in the vibrations of electrons about fixed positions in the atom, thus, seemingly, completing the chain of evidence in favor of the electromagnetic theory of light and confirming the hypothesis resulting from the Lorentz theory of dispersion (Sec. 5, this chapter).

8. "Photoelectrons."—We can now return to the question raised at the end of Sec. 3 of this chapter: What are the carriers of electricity in the photoelectric current? The discovery of the electron seemed to furnish an answer: *The photoelectric effect is due to the liberation, from the illuminated metal plate, of electrons which, under the influence of the electric field, pass from cathode to anode*, thereby causing the photoelectric current. This hypothesis was confirmed by the experiments of Lenard[1] and of Mer-

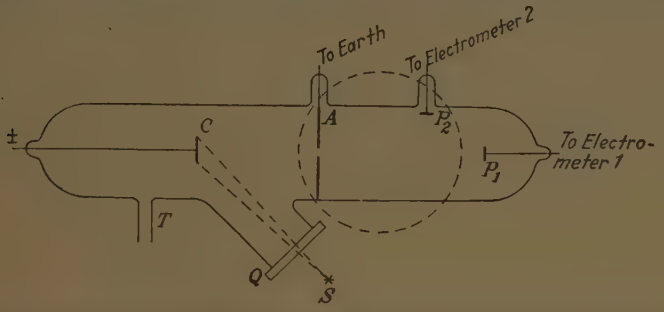

FIG. 35.—Lenard's apparatus for determining the ratio e/m for photoelectrons.

ritt and Stewart,[2] who proved independently that the photoelectric discharge is deflected in a magnetic field, exactly as are cathode rays. And Lenard, by measuring the deflection of the "photoelectric rays" in a known magnetic field, found a value of e'/m of (about) 1.2×10^7, in approximate agreement with Thomson's value of e'/m for electrons. Later work by Alberti[3] gave a value of e'/m for photoelectrons of 1.765×10^7 e.m.u. per gram.

Lenard's method of determining e/m for photoelectrons is particularly instructive. The apparatus used is shown diagrammatically in Fig. 35. A glass tube, which may be exhausted to the highest attainable vacuum through the side tube T, contains an aluminum cathode C, which may be illuminated by ultraviolet light from a spark S, the light passing through the quartz

[1] *Ann. Physik*, vol. 2, p. 359 (1900).
[2] *Phys. Rev.*, vol. 11, p. 230 (1900).
[3] *Ann. Physik*, vol. 39, p. 1133 (1912).

plate Q. C may be charged to any potential, positive or negative. A screen A, which has a small hole at its center and which is connected to earth, serves as anode. P_1 and P_2 are small metal electrodes connected to electrometers. When C is illuminated and charged to a negative potential of several volts, photoelectrons are liberated and accelerated toward the anode A. A few electrons pass through the hole in the center of A and proceed, thereafter at uniform velocity, to the electrode P_1, their reception there being indicated by the electrometer *1*. But if, by means of a pair of Helmholtz coils (represented by the dotted circle), a magnetic field directed toward the reader is produced in the region between A and P_1, the electrons will be deflected upward in a circular path and, with a sufficient field strength, will strike the electrode P_2.

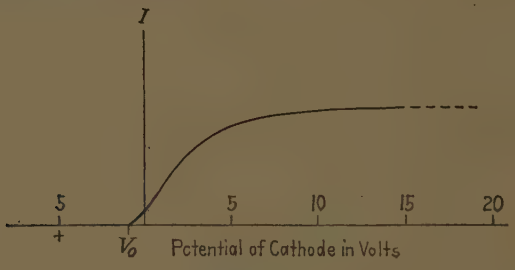

FIG. 36.—Variation of photoelectric current with variation of potential of cathode.

Lenard first investigated the relation between the current reaching the anode and the potential V applied to C. There was no photoelectric current when V was several volts positive. But when V was dropped to about 2 volts *positive*, a small current was observed. This indicated that the photoelectrons were not simply *freed* from the cathode but that some of them, at least, *were ejected with sufficient velocity to enable them to overcome the retarding potential* of 2 volts. The current increased when V was reduced to zero and increased still more rapidly as V was made negative; but attained a "saturation" value after V had reached some 15 or 20 volts, negative. These data are shown diagrammatically in Fig. 36. I is the photoelectric current, and V_0 is the positive potential (about 2 volts) which it is necessary to apply to the cathode to prevent the escape of any electrons.

The determination of e'/m was made essentially as follows: Let a negative potential V, large compared to V_0, be applied

to the cathode. The photoelectron, on reaching the anode, will have a kinetic energy given by

$$Ve' = \tfrac{1}{2}mv^2 \tag{27}$$

where e' and m are the charge and mass of the electron, and v its velocity on reaching A (Fig. 35). Assuming that after leaving A the electron moves in a uniform magnetic field, the circular path which the electron follows is determined by the equation

$$He'v = \frac{mv^2}{R} \tag{28}$$

where H is the strength of the magnetic field just necessary to cause the electron to reach P_2, and R is the radius of the corresponding circular path, determined from the geometry of the apparatus. Eliminating v between equations (27) and (28), and solving for e'/m, we have

$$\frac{e'}{m} = \frac{2V}{H^2R^2} \tag{29}$$

The quantities V, H, and R being known, e'/m may be computed; and v may then be determined from either equation (27) or equation (28). In this way, Lenard measured the values of e'/m for a wide range of values of V. Some of his results are shown in the following table:

V in volts	e'/m e.m.u. per gram	Velocity, centimeters per second
607	1.17×10^7	12×10^8
4,380	1.12	32
12,600	1.18	51

The ratio e'/m is observed[1] to be constant over a wide range of potentials applied to the cathode. It is, also, to be noted that the velocity attained by the electrons is, for the higher voltages, a substantial fraction of the velocity of light.

9. Relation between Photoelectric Current and Intensity of Illumination of the Cathode.—The experiments of Elster and Geitel,[2] Lenard,[3] and Ladenburg[4] seemed to show that, so long

[1] As pointed out above, more recent determinations give a higher value for e'/m for photoelectrons.

[2] *Ann. Physik*, vol. 48, p. 625 (1893).

[3] *Ann. Physik*, vol. 8, p. 154 (1902).

[4] *Ann. Physik*, vol. 12, p. 573 (1903).

as there was no change in the spectral quality of the light causing the emission of electrons, the photoelectric current was apparently proportional to the intensity of illumination on the emitting surface. But some experiments by Griffith[1] threw doubt on this conclusion.

In 1909, the author reported measurements[2] on the relation between the photoelectric current and light intensity, in which a sodium surface in vacuum (the so-called "photoelectric cell") was used with an electrometer as the current-measuring instrument for low intensities (up to 0.5 foot-candles), and a sensitive d'Arsonval galvanometer for high intensities (up to 600 foot-candles). The results showed that both for low intensities and for high intensities the photoelectric current is strictly proportional to the intensity of illumination. This conclusion was confirmed by the later experiments of Elster and Geitel,[3] who found the linear relation to hold over a very wide range of intensities (50,000,000:1). Kunz and Stebbins found a similar proportionality over the range of illuminations: 0.018 meter-candle to 1,110 meter-candles. This law of proportionality seems, therefore, to be well established.

Now, each electron, photoelectrically emitted, carries a charge e; and if the photoelectric current be I, the number of electrons emitted per second is I/e. Since experiment shows that I is strictly proportional to the intensity of illumination, it follows that *the rate of emission of photoelectrons is strictly proportional to the intensity of illumination.*[4] This is one of the very important laws of the photoelectric effect.

10. Velocity Distribution Curves for Photoelectrons.—The relation between photoelectric current and the potential applied to the cathode, as in the experiments of Lenard (see Fig. 36), has been the subject of many investigations[5] and has lead to results of extraordinary importance. The principle of the

[1] *Phil. Mag.*, vol. 14, p. 297 (1907).

[2] *Phys. Rev.*, vol. 29, pp. 71, 404 (1909).

[3] *Phys. Zeitsch.*, vol. 14, p. 741 (1913); vol. 15, p. 610 (1914); and vol. 17, p. 268 (1916).

[4] The variation in photoelectric current with wave length of the incident light, for a constant energy flux onto the emitting surface, has been the subject of many investigations. For a discussion of this subject, the reader is referred to ALLEN'S "Photoelectricity."

[5] For the general method and technique see the experiments of RICHARDSON and COMPTON, *Phil. Mag.*, vol. 24, p. 575 (1912).

methods employed is illustrated diagrammatically in Fig. 37. The emitting electrode C and the receiving electrode A are enclosed in a highly evacuated bulb of glass or of glass with quartz window, through which C may be illuminated. C is connected to the slider S of a potentiometer wire, one point P of which is connected to earth and is, therefore, at zero potential. The potential of C may, thus, be made either positive or negative. The receiving electrode A is connected to earth through a sensitive current-measuring instrument G, usually an electrometer. In order to prevent an inverse photoelectric current from A to C, due to reflected light reaching A when C is positive,

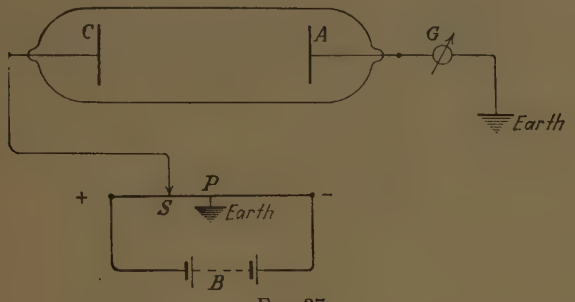

FIG. 37.

A is frequently chosen of such material as to be photoelectrically insensitive to the spectral region used to illuminate C. This necessitates a correction for the "contact" potential difference between C and A. In order to eliminate errors due to reflection of electrons and to unsymmetrical emission of electrons from C, Richardson and Compton placed C at the center of a spherical bulb silvered on the inside except for a small area through which light might be admitted. This silvered surface served as receiving electrode A.

After eliminating all spurious effects, and illuminating the emitting electrode C *with strictly monochromatic light*, the intensity E of which can be varied in a known manner, the relation between the photoelectric current I and the potential V is as shown in Fig. 38. Thus, let the intensity of illumination be E_1. No photoelectric current is observed when the *positive* potential is greater than a critical potential $+V_0$. At potentials just less than $+V_0$, a small current is observed, and as the potential decreases from $+V_0$ to zero, the current rises rapidly to a

maximum value I_1, which it reaches when $V = 0$. *No further increase in I is observed when V becomes negative.* I_1 is, therefore, the *maximum* current resulting from illumination (at this particular wave length) of intensity E_1. If the intensity of illumination be doubled, *i.e.*, E_2, a curve of the form *2* is obtained. The maximum current I_2 is exactly double the current I_1, but *the critical potential V_0 is exactly the same as for the illumination E_1.* Increasing the intensity of illumination to E_3 or E_4 increases the corresponding maximum current proportionately *but causes no change whatever in V_0.* Calling this maximum current I_m for a

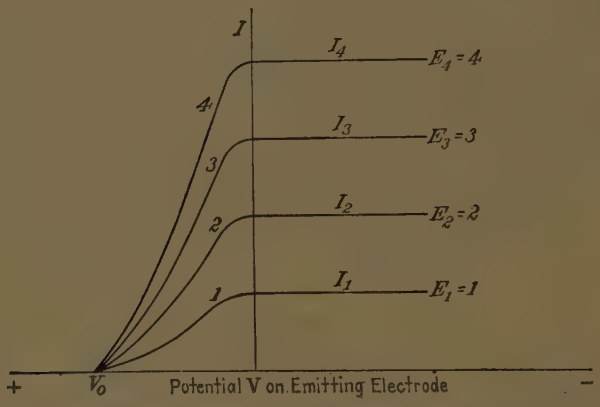

FIG. 38.—Variation, with potential, of the photoelectric current from a cathode when illuminated by different intensities E_1, E_2 . . . of *monochromatic* radiation.

given intensity of illumination E, we have, as shown in Sec. 9 of this chapter,

$$I_m \propto E \qquad (30)$$

Indeed, if the ordinates of curves *2*, *3*, and *4* be divided by 2, 3, and 4, respectively, the resulting curves would coincide with curve *1*.

These facts are readily interpreted on the assumption that the electrons are emitted *from the surface of the electrode* with initial velocities v varying from a certain maximum velocity v_m, corresponding to the critical potential V_0, down to zero velocity. For, if v is the velocity with which an electron, mass m, is emitted, its kinetic energy, therefore, being $\frac{1}{2}mv^2$, it is obvious

that only those electrons will reach the receiving electrode A (Fig. 37) for which[1]

$$\tfrac{1}{2}\, mv^2 > Ve \qquad (31)$$

where V is the potential difference between the plates C and A, and e is the charge on the electron. Electrons emitted with smaller velocities do not possess sufficient energy to reach A, and they, therefore, "fall" back to the plate C, just as a ball, thrown upward from the surface of the earth, is pulled back to the earth by the force of gravity. Accordingly, if the current is I_1 (Fig. 39) when the potential difference is V_1, I_1/e electrons (per second)

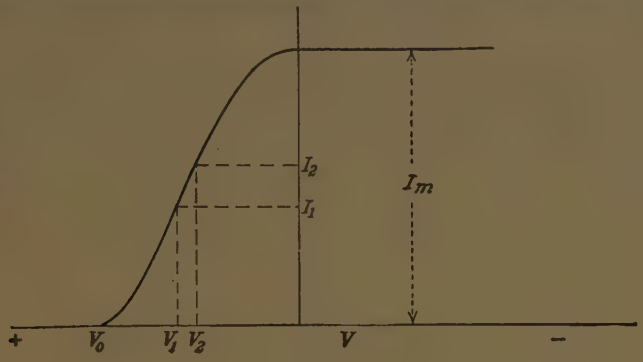

FIG. 39.

leave the plate C with velocities in excess of v_1, where v_1 is determined by $V_1 e = \tfrac{1}{2} m v_1^2$. If the potential be reduced, by a small amount ΔV, to V_2, the current increases, by a small amount ΔI, to I_2. Therefore, $\Delta I/e$ electrons per second leave the plate with velocities between the limits v_1 and v_2, which are defined by

$$V_1 e = \tfrac{1}{2}\, m v_1^2$$
$$V_2 e = \tfrac{1}{2}\, m v_2^2$$

In other words, the *slope* of the curve at any point, in Fig. 39, is proportional to the *number* of electrons possessing energies corresponding to the value of V at that point. Since, when the applied potential $V_m > V_0$, no current is observed, *the maximum velocity v_m possessed by any photoelectron is given by*

$$\tfrac{1}{2}\, m v_m^2 = V_0 e \qquad (32)$$

[1] Strictly speaking v in equation (31) is not the actual velocity of the photoelectron, but is the component of the velocity in the direction of the electric field. In the above mentioned experiments of Richardson and Compton (small spherical emittor at the center of a comparatively large spherical receiving electrode) v is very nearly the actual velocity.

When $V = 0$, *any* electron freed with any velocity greater than zero reaches plate A, and, since for small negative (*i.e.*, accelerating) values of V, there is no further appreciable increase in the photoelectric current, it follows that small electric fields play no appreciable part *in initially freeing the electrons from the plate.*[1] And the total number of electrons (per second) freed from the plate C is given by I_m/e, where I_m is the photoelectric current for any negative value of V. Curves of the kind shown in Figs. 38 and 39 are sometimes referred to as "velocity-distribution curves," although, correctly speaking, the velocity-distribution curves would be those in which the *slopes* of these curves are plotted as ordinates against the velocity v, determined from $Ve = \frac{1}{2}mv^2$, as abscissæ.

11. Relation between the Velocities of Photoelectrons and the Frequency of the Light.—If the photoelectric current as a function of applied voltage V be determined for several different monochromatic radiations of wave length λ_1, λ_2, λ_3, etc., falling on the emitting electrode, curves of the form shown in Fig. 40 result, in which the intensities of illumination for each wave length have been so adjusted as to give the same value of I_m in each case. Here $\lambda_1 > \lambda_2 > \lambda_3$, but $V_1 < V_2 < V_3$, where V_1, V_2, and V_3 are the corresponding critical retarding voltages. This means that the shorter the wave length the greater is the

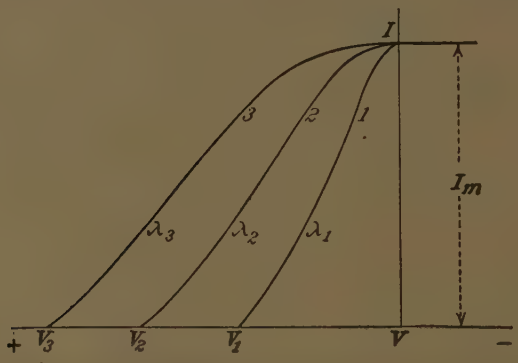

FIG. 40.—Dependence of photoelectric current on wave lengths of the exciting light: $\lambda_1 > \lambda_2 > \lambda_3$

[1] Of course, if V is positive, it may *cause the return* to the electrode C of some or all of the photoelectrons. And if V is negative, it may *accelerate* them toward the plate A so that they reach A with a *greater* velocity than that with which they left the plate. If V has a large negative value secondary effects are produced which complicate the *observed* phenomena.

retarding voltage V_0 just necessary to prevent the escape of the "fastest" electron. Or the maximum kinetic energy[1] of photoelectrons, given by $\frac{1}{2}mv^2 = V_0 e$, *increases with increasing frequency* ν *of the light which causes their emission.*

A very simple linear relation has been found to exist between this maximum energy of emission and the frequency of the light. If, as shown by Millikan, a curve be plotted between $V_0 e$ and the corresponding frequency ν of the light, there results the straight line, shown in Fig. 41, which has an intercept ν_0. The experimental meaning of this intercept is that light of frequency less than ν_0 cannot cause the emission of photoelectrons from the metal concerned. ν_0 is characteristic of the emitting electrode, but *the slope of the curve is the same for all electrodes.* The equation of the curve may be written:

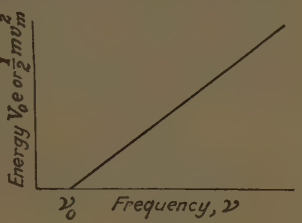

FIG. 41.—Relation of maximum energy of photoelectrons to frequency of the exciting radiation.

$$V_0 e = \tfrac{1}{2}mv_m^2 = h(\nu - \nu_0) = h\nu - h\nu_0$$

or

$$\tfrac{1}{2}mv_m^2 = h\nu - \omega_0 \qquad (33)$$

where h is the slope of the curve and ω_0 is written for $h\nu_0$.

Now, since the dimensions of the left-hand side of equation (33) are those of energy, both terms on the right-hand side must, likewise, stand for quantities of energy. Since h, the slope of the curve, is independent of the nature of the emitting electrode, the quantity of energy $h\nu$ *depends only on the frequency of the incident light.* On the contrary, ω_0 is a quantity of energy characteristic of the emittor and is independent of the light. It is, therefore, natural to interpret equation (33) by saying the $h\nu$ is the energy which the light of frequency ν gives to the electron and that ω_0 is

[1] The careful work of Millikan (*Phys. Rev.*, vol. 7, p. 355 (1916)) showed that if the radiation be truly monochromatic, at least if it contained no wave lengths shorter than the wave length λ for which a given curve is being determined, the curve approaches the voltage axis at a finite angle, and *not* asymptotically. Failure to exclude stray light of short wave length is apparently the explanation of the contradictory result of Ramsauer (*Ann. Physik*, vol. 45, pp. 961 and 1121 (1914)), who, by deflecting the photoelectrons in a magnetic field, somewhat after the manner of Lenard's experiments (p. 155), thereby producing a "magnetic spectrum" of velocities, made a direct determination of the distribution of velocities. The reader will find Ramsauer's *method* of procedure instructive.

the part of this energy which the electron expends in escaping from the emittor; the remainder, $\frac{1}{2}mv_m^2$, is the kinetic energy with which the electron is actually *observed*[1] to leave the emittor.

If, in Fig. 41 (and equation (33)), the ordinates be expressed in ergs and the abscissæ in vibrations per second, the numerical value of h is found to be[2] 6.56×10^{-27}. This constant h, called, for reasons to be explained later, "Planck's constant," is one of the fundamental constants of nature and has played an extraordinary part in modern physics. *The product $h\nu$ is called a quantum of energy corresponding to light of frequency ν.*

At first thought, it might seem that the above discussion leading to equation (33) applied only to those photoelectrons which possess the *maximum* velocity v_m, *i.e.*, to those electrons corresponding to the critical retarding voltage V_0, and that a lesser quantity of energy than $h\nu$ is given to those electrons which are observed to possess smaller energies. But, as we have pointed out above, the *observed* velocities are those possessed by the electrons *after* they have left the emittor and, for the swiftest electrons, it requires an amount of energy ω_0 to "free the electron" from the surface of the emittor. It is, therefore, just as logical to assume that those electrons which are observed to possess velocities *smaller* than v_m have required energies *larger* than ω_0 to free them from the emittor *and that each electron initially receives, as a result of the photoelectric process, an amount of energy $h\nu$.* Indeed, this latter view is much the more logical, since we can readily account for this increased amount of energy required to escape from the metal by assuming that light penetrates a finite distance into the metal, through many surface layers of atoms, and that, in general, the photoelectrons originating beneath the surface lose some of their energy by collisions before they reach the surface. Only those which originate right at the surface escape with the maximum energy $h\nu - \omega_0$. We may assume, therefore, that the equation

$$\frac{1}{2}mv_m^2 = h\nu - \omega_0 \qquad (33)$$

is generally applicable to *all* photoelectrons and that, were it not for these accidental collisions, before reaching the surface of the emittor, every photoelectron would possess the same velocity v_m.

This equation (33) has had a very interesting history and is one of the most fundamental equations, or laws, of modern

[1] See note page 161.

[2] MILLIKAN: "The Electron."

physics. It is frequently referred to as "Einstein's photoelectric equation," since it was first proposed by Einstein,[1] in 1905, as a result of the extension to the photoelectric process of the concept previously developed by Planck (see Chap. VII), that interchanges of energy between radiation and matter take place in energy quanta $h\nu$, where ν is the frequency of the radiation absorbed or emitted and h is a constant. Einstein had at his disposal only qualitative data to show that his equation gave results of at least the right order of magnitude. Two years later, Joffé[2] pointed out that some data, previously reported by Ladenburg[3] as indicating that the *velocity* of the photoelectrons is proportional to frequency, were in at least as good agreement with Einstein's equation, which states that the square of the velocity is proportional to (rather, a linear function of) the frequency. From this data of Ladenburg, Joffé computed that the constant h in Einstein's equation was about 3×10^{-27} erg $\times$ sec. This was one of the very first photoelectric determinations of h. The equation received final and complete experimental verification as a result of the precision experiments of Millikan,[4] to which reference has been previously made. More recent work has extended the validity of the equation to the X-ray region, where frequencies are involved which are several thousand times the frequencies of the visible and near-ultra-violet light for which Millikan's verification was made. Indeed, Einstein's photoelectric equation is, in many respects, to the modern quantum theory what Newton's second law of motion, *i.e.*, $F = ma$, is to mechanics. But in spite of its generality and of the many successful applications which have been made of it in recent theories in physics, the equation is, as we shall see presently, based on a concept of radiation—the concept of "light quanta"—so completely at variance with the most fundamental postulates and conclusions of the electromagnetic theory of radiation that all attempts at reconciliation between the two theories have, *so far*, failed. We shall return to this question in Sec. 15 of this chapter.

12. Origin of the Photoelectrons.—If the phenomenon of the conduction of electricity in metals be ascribed to the presence in

[1] *Ann. Physik*, vol. 17, p. 132 (1905).
[2] *Ann. Physik*, vol. 24, p. 939 (1907).
[3] *Phys. Zeitschrift*, vol. 8, p. 590 (1907).
[4] *Phys. Rev.*, vol. 7, p. 355 (1916).

the interatomic spaces of the so-called "free" electrons, then we may recognize two classes of electrons in metals: (1) these "free" electrons and (2) the "bound" electrons, *i.e.*, those which are attached to, or are a part of, the atoms of the metal. The question then arises: Do the photoelectrons come from the free electrons or from the bound electrons?

One line of attack on this question is the influence of temperature on the photoelectric process. As the temperature of a (solid) substance rises, the energy of agitation of its constituent molecules or atoms increases proportionally to the absolute temperature; and, correspondingly, the energy of translation of the electrons in the "free electron atmosphere" increases. This increase in translational velocity is the basis of the explanation of the increase in electrical resistance of metals with increasing temperature. If the temperature be raised sufficiently high, the translational energy of some of these free electrons may become sufficient for them to escape from the surface of the metal, in much the same way as molecules of a liquid escape through the surface of the liquid in the process of evaporation; and we then have the well-known thermionic emission of electrons. Now, if the photoelectrons come from the free electrons in the metal, we should expect that either the number of the photoelectrons or their velocities, or both, would depend, in some way, on temperature. For example, if the kinetic energy of the free electrons increases with rise of temperature, as both the variation of resistance with temperature and thermionic emission seem to indicate, it should be easier for the light to cause the ejection of photoelectrons at higher temperatures than at lower, and light of a given intensity might cause the emission of more electrons at the higher temperature.

On the contrary, if the photoelectrons come from the atoms of the metal, one might expect that the photoelectric process should be practically independent of temperature, since there is no reason for believing that the *internal* energy of an atom depends on temperature, at least until comparatively high temperatures be reached.

There have been numerous investigations of the effect of temperature on photoelectric phenomena, at first with conflicting results. Thus, Hoor[1] found that the photoelectric effect in zinc

[1] *Wien Berichte*, vol. 97, p. 719 (1888).

was less at 55°C. than at 18°C., while Stoletow[1] found that the activity of platinum increased when it was heated to 200°C. Elster and Geitel[2] found that the photoelectric discharge from zinc was independent of temperature but that in the case of potassium, there was an increase in activity up to 60°C.; while Zeleny[3] found, with platinum, first a decrease to a minimum and a subsequent increase as the temperature was raised to several hundred degrees centigrade, where the true photoelectric effect began to be masked by thermionic emission.

These early experiments were probably vitiated by the secondary effect of gases or of electropositive impurities in changing the condition of the photosensitive surface. For, contrary to the above cited results of Elster and Geitel on potassium, Dember[4] and Kunz[5] found no change of the photoelectric effect with the alkali metals when they were in a very high vacuum. This result is in entire agreement with the experiments of Ladenburg[6] and of Millikan and Winchester.[7] The latter investigators worked with many different metals as emittors (copper, gold, iron, lead, aluminum, etc.) over a temperature range from 25°C. to 125°C. Neither total photoelectric current nor velocity of emission was found to depend on temperature within the limits of accuracy of the experiments—1 or 2 per cent.

Some recent experiments, particularly at low temperatures, indicate that the photoelectric current does depend on temperature,[8] but the most reasonable interpretation of these results seems to be that temperature change produces an alteration in the surface of the metal so as to change the amount of work ω_0 necessary for the escape of the electron from the metal but that there is no change in the amount of energy $h\nu$ which the electron initially receives.

This evidence points clearly to the conclusion that, when all spurious effects are eliminated, the photoelectric process, both as to number of photoelectrons and their velocities, is independent

[1] *Comp. rend.*, vol. 108, p. 1241 (1889).
[2] *Ann. Physik*, vol. 48, p. 634 (1893).
[3] *Phys. Rev.*, vol. 12, p. 321 (1901).
[4] *Ann. der Physik*, vol. 23, p. 957 (1907).
[5] *Phys. Rev.*, vol. 29, p. 174 (1909).
[6] *Verhandlungen der Deutsch. Phys. Gesell.*, vol. 9, p. 165 (1907).
[7] *Phil. Mag.*, vol. 14, p. 188 (1907).
[8] See the experiments of IVES, *Jour. Opt. Soc. Amer.* and *Rev. Sci. Inst.*, vol. 8 p. 551 (1924).

of temperature *and that, therefore, the photoelectrons come from the atoms of the emittor* rather than from the free electrons.

This conclusion receives confirmation in the beautiful experiments of Robinson[1] on the photoelectric effect of X-rays (see Chap. XII), which cause the ejection from an emittor of several groups of photoelectrons, each group having a different maximum velocity v_m— a circumstance explainable only if the electrons originate at different "depths" within the *atom*, thereby requiring different quantities of energy to escape from the atom.

Further, it can be shown that, whatever the nature of the photoelectric process, the laws of the conservation of energy and of momentum require that the photoelectron should originate in an atom, *i.e.*, that a *free* electron cannot be given a quantum of radiation.

We must, therefore, base any explanation or theory of the photoelectric process on the experimental conclusion that the atom, by a mechanism at present quite unknown, but *probably* as a result of absorption of energy from light of frequency ν, causes the emission of one (or more) of its electrons with an energy $h\nu$, part of which may be used to escape from the atom itself and part from the surface of the emittor, the remainder appearing as kinetic energy of the photoelectron.

13. Source of the Photoelectric Energy.—(*a*) In the last paragraph of the preceding section, we stated that *probably* the atom absorbs from the incident light the energy used in expelling a photoelectron. Let us examine this question in more detail. The following is a summary of the pertinent experimental conclusions, previously discussed:

1. For a given spectral composition of the incident light, the *number* of photoelectrons expelled per second is strictly proportional to the intensity of the light, over a very wide range of intensities. Thus, let n be the number of electrons emitted per square centimeter per second by light of intensity I. Then,

$$n = kI \tag{34}$$

where k is a constant, which depends on the frequency of the light and the nature of the emittor.

[1] *Proc. Roy. Soc.* (*London*), vol. 104, p. 455 (1923); and *Phil. Mag.*, vol. 53. p. 241 (1925).

2. The kinetic energy of the photoelectrons is a linear function of the frequency of the light, the relation between the two being given by the Einstein photoelectric equation:

$$\tfrac{1}{2}mv^2 = h\nu - \omega_0$$

And, with the interpretation of ω_0 as the amount of work required to escape from the emittor, it follows that each electron receives, initially, an amount of energy, $h\nu$, which is strictly proportional to the frequency of the incident light *and is independent of the nature of the emittor.*

3. The kinetic energy of the photoelectrons, $\tfrac{1}{2}mv_m^2$, emitted by monochromatic light has been found to be *rigorously independent* of the intensity of the light over a very wide range of intensities.

From experimental conclusion 1, it follows, at once, that *the rate* dE_P/dt *at which energy is given to photoelectrons per square centimeter of emitting surface is strictly proportional to the intensity* I *of the light.* That is,

$$\frac{dE_P}{dt} = k \cdot I \tag{35}$$

Now, when light is incident onto a metallic surface, it is partly reflected and partly absorbed; and *the rate* dE_A/dt *at which energy is absorbed, per square centimeter, is strictly proportional to the intensity of the light, i.e.,*

$$\frac{dE_A}{dt} \propto I \tag{36}$$

and, therefore,

$$\frac{dE_P}{dt} \propto \frac{dE_A}{dt} \tag{37}$$

The presumption is very strong, therefore, that the energy acquired by the photoelectrons is obtained from the incident light. In fact, the initial energy acquired by the photoelectrons seems to be determined *solely by the light* and *not at all by the emittor.*

(*b*) At first thought, it might seem (1) that this conclusion is inconsistent with the fact that the kinetic energy of each photoelectron is proportional to the frequency ν and (2) that therefore the photoelectric process might be a resonance phenom-

enon whereby the light functions simply as a "trigger," releasing the photoelectron with an amount of energy which it already possessed in the atom. To illustrate by analogy:

One can readily imagine an electromechanical device in which a metal diaphram is set into vibration, when sound of a particular frequency strikes it, with sufficient amplitude to close an electric circuit, which, in turn, pulls a trigger which discharges a rifle. In this case, the *energy* with which the bullet leaves the rifle comes from the powder and does not depend on the intensity of the sound. This coincides with experimental conclusion 3, above. One can, then, imagine a series of such mechanisms, each tuned to a different frequency, in which the amount of powder in each rifle is so adjusted that the energy with which the bullet leaves the rifle is proportional to the frequency of the sound which sets it off. This would coincide with experimental conclusion 2, above. Applying this "trigger" theory to the photoelectric process, we should require that each photoelectric emittor contained resonating systems of all frequencies, from the frequency of the long wave length photoelectric limit to (theoretically) infinite frequencies, and that each of these resonators, when "set off" by light of appropriate frequency, should expel an electron with an energy proportional to the frequency. All this involves quite too much of an "*ad hoc*" assumption. And even if the resonance theory were tenable, we should then have to explain (see experimental conclusion 1, above) why the *number* of the photoelectrons is strictly proportional to the *intensity* of the light. (In our analogy, it does not follow that the *number* of rifles discharged per second is proportional to the intensity of the sound.)

The facts, therefore, seem to demand the conclusion that the photoelectric energy comes directly from the light and *not* from energy previous stored up in the atom and released by a resonance, or "trigger," effect.

14. What Is the Photoelectric Mechanism?—If the photoelectrons come from the atom, and if the energy necessary for the expulsion of the electrons comes from the incident light, it must be that the atom absorbs the energy from the light and gives this energy to the photoelectron. But how can we picture an atomic mechanism which will function in accordance with the experimental facts? The difficulties in the way of postulating such a mechanism, particularly on the basis of the classical electro-

magnetic wave theory of light, can best be shown by some numerical data:

1. A photoelectric current of 1×10^{-12} e.m.u. per square centimeter is easily obtained from a sodium surface *in vacuo* with very moderate intensity of illumination. Taking the value of the charge on the electron as 1.592×10^{-20} e.m.u., this current corresponds to the emission of 6.28×10^{7} electrons per square centimeter per second. These electrons come from the surface layers of atoms. And we can easily compute the order of magnitude of the number of atoms involved. For, calling Avogadro's number N (*i.e.*, the number of atoms per gram-atom), the atomic weight of the emittor A, and its density δ, the number of atoms per unit volume n is given by

$$n = \frac{N}{A}\delta$$

$N = 6.06 \times 10^{23}$; and for sodium, $A = 23.0$ and $\delta = 0.97$ grams per cubic centimeter. Therefore, $n = 25.5 \times 10^{21}$ atoms per cubic centimeter. Assuming the atoms in a centimeter-cube of sodium to be arranged in regular rows, columns, and layers,[1] one finds that there are $\sqrt[3]{25.5 \times 10^{21}} = 2.95 \times 10^{7}$ atoms along each edge, or $(2.95 \times 10^{7})^2 = 8.7 \times 10^{14}$ atoms in a layer 1 sq. cm. in area and 1 atom deep. Assuming, for the sake of computation, that the photoelectrons are supplied by, say, the first 10 layers of atoms, we find that 8.7×10^{15} atoms furnish, under the conditions of illumination above mentioned, 6.26×10^{7} electrons per second. That is, 1 atom in $\frac{8.7 \times 10^{15}}{6.28 \times 10^{7}} = 1.38 \times 10^{8}$, on the average, furnishes 1 photoelectron per second. But what is it which determines *which one* of these hundred million odd atoms shall furnish an electron in any particular second? According to the wave theory of light, radiant energy should be distributed continuously over the wave front. Save for differences in thermal agitation, we know of no reason to expect that one atom differs from another in any way which might result in one atom having at any instant a greater absorbing power than another. And thermal agitation cannot be responsible for differences among atoms if the photoelectric effect be independent of temperature. Apparently, we are unable, on the basis of

[1] The crystal structure of sodium is really a body-centered cube. See International Critical Tables, vol. I, p. 340.

the classical theory of radiation, to put forward any hypotheses which should result in singling out the one atom in a hundred million.

2. But the difficulties in which the classical theory finds itself in attempting to explain the experimentally well-established facts of the photoelectric phenomenon are, perhaps, even more clearly brought out by an attempt to compute how long, on the classical theory, it should take an atom to absorb enough energy to emit a photoelectron. An intensity of illumination of 0.1 meter-candle, falling onto a sodium surface, produces an easily measurable photoelectric current. This illumination corresponds to an energy flux of several ergs (say, ten[1]) per square centimeter per second, depending on the light source. Only a little over 1 per cent of this energy falls within the limit of the visible spectrum, and a much smaller proportion, certainly not over 0.05 erg per square centimeter per second, falls within the spectral range effective in expelling photoelectrons from sodium, which is sensitive in the blue and near-ultra-violet part of the spectrum. Sodium has a high reflecting power, and, since only *absorbed* energy can possibly be used in expelling electrons, we conclude that not over 0.001 erg per square centimeter per second is available for the photoelectric process.

According to the electromagnetic theory, this absorbed energy, 0.001 erg per square centimeter per second, should be equally distributed among the 8.7×10^{15} atoms which form the (10, arbitrarily assumed) surface layers. That is, each atom should absorb

$$\frac{0.001}{8.7 \times 10^{15}} = 1.1 \times 10^{-19} \text{ ergs per second}$$

Now, a quantum of light corresponding to $\lambda = 0.00004$ cm. (violet light) is

$$\begin{aligned} h\nu &= 6.55 \times 10^{-27} \times 0.75 \times 10^{15} \\ &= 5 \times 10^{-12} \text{ ergs} \end{aligned}$$

This, therefore, is the energy which the atom gives to the electron as a result of the photoelectric process involving light of this wave length. If the atom obtains this energy by absorption from the incident light, the number of seconds required for the

[1] Assuming tungsten light and taking the efficiency of the 40-watt vacuum tungsten lamp as 10 lumens per watt. (See CADY and DATES: "Illuminating Engineering," John Wiley & Sons, Inc., 1925.)

atom to obtain enough energy to expel an electron would be given by

$$\frac{5 \times 10^{-12}}{1.1 \times 10^{-19}} = 4.5 \times 10^{7} \text{ seconds}$$

This is over 500 days!

In other words, if a sodium surface be illuminated by a tungsten lamp, the intensity of illumination being 0.1 meter-candle, it should require several hundred *days* of continuous illumination before a photoelectric current starts to flow, *if we assume*

1. that the photoelectron comes from the atom;
2. that the atom absorbs from the incident light the energy required to expel the electron;
3. that each atom in the surface layers of the photoactive material absorbs only its own proportionate quota of energy—as seems to be required by the wave theory of light.

But there has never been observed any time lag between the beginning of illumination and the starting of the photo-electric current. Indeed, some recent measurements[1] show that, if there be such a time lag, it is less than three billionths of a second. Clearly, one (or more) of these three assumptions just stated must be wrong, since the experimental facts and the numerical data on the basis of which the computation is made seem to be well founded.

The classical electromagnetic theory of light, therefore, not only gives us no clue as to the mechanism by which photoelectric emission occurs, but, also, it seems to be in direct conflict with well-established experimental facts, which facts point unmistakably to some kind of discontinuity or "structure" to what, heretofore, we have called a "wave front."

15. The Photoelectric Effect and the Corpuscular Theory of Light.—If we could dismiss the phenomenon of interference of light and the deductions therefrom, both experimental and theoretical, and if, with Newton, we could return to the corpuscular theory, the difficulties raised in the preceding section could be easily explained, at least qualitatively. Thus, on the corpuscular theory, we might regard a beam of light as a "rain" of corpuscles of energy. When such a "shower" of light falls on the sodium surface, only here and there an atom is being

[1] LAWRENCE and BEAMS: *Phys. Rev.*, vol. 29, p. 903 (1927).

struck by a corpuscle at any given instant. If, now, we assume (1) that each corpuscle, or "quantum" in modern terms, possesses energy $h\nu$ and (2) that, by some unknown process, a "collision" between a quantum and an atom may, under suitable circumstances likewise quite unknown, result in the absorption of the whole quantum by the atom and the subsequent emission of the photoelectron with the initial energy $h\nu$, we can, at once, explain why only one atom in many millions expels an electron in any particular second and, also, why there is no time lag in the photoelectric process.

Such a theory would predict, also, that the photoelectric current should be proportional to light intensity, as is experimentally observed. For, the intensity of the light should be proportional to the number of quanta falling per second on each square centimeter of the photoelectric emittor; and, because of the large number of quanta and of atoms involved, the proportion of collisions between quanta and atoms which result in the emission of an electron should be constant.

Further, we should have a ready explanation of the experimentally observed facts: (1) that the initial velocity of the photoelectrons is independent of the intensity of the light and (2) that this velocity depends only on the wave length of the light. For, keeping the wave length of the incident light constant and increasing the intensity would increase the *number* of quanta striking each square centimeter each second and, proportionately, the number of collisions resulting in photoelectric emission; but there would be no change in the *nature of each collision:* Each photoelectron would, at the higher intensity of illumination, receive *exactly* the same energy, $h\nu$, as at the lower intensity. If the *frequency* of the incident light be increased, however, the value of $h\nu$ is increased, and, accordingly, the energy received by each photoelectron would be increased. The Einstein photoelectric equation

$$\tfrac{1}{2}mv^2 = h\nu - \omega_0$$

follows, at once.

The difficulties with such a radical theory of light are many. For example, if we regard light, incident onto a surface, as a "shower" of corpuscles or quanta of energy, what can possibly be the meaning of *frequency* in connection with such a phenomenon? There is nothing periodic about a falling raindrop, unless we think of the drop as in revolution about an axis through its

center of gravity as it falls, the speed of this angular rotation determining the frequency, and the distance fallen during 1 revolution being a "wave length." Nevertheless, frequency plays a very fundamental role in determining the energy $h\nu$ of the quantum. It should be pointed out, however, parenthetically, that we do not measure *directly* the frequency of a light ray. We *measure* (1) the velocity c of the light and (2) its wave length (λ), *on the assumption that light is a wave motion*, and then we *compute* the frequency ν by the equation

$$c = \lambda\nu$$

We have to rely on the wave theory of light to give us the energy value $h\nu$ of a quantum!

And there still remains the phenomenon of interference, which, since its discovery by Young, in 1802, has defied explanation on any other basis than by assuming light to be a wave motion. However, the experimental facts of photoelectricity are equally as cogent as is the phenomenon of interference, and *they cannot be explained on the basis of the present wave theory* of light. Here, then, is the most perplexing question of modern physics, a question which physicists have been trying to answer for 2½ centuries: Is light undulatory or corpuscular? In spite of the vast amount of data bearing on the subject, we, today, are apparently no more able to give a *categorical* answer to this question than were Huyghens and Newton.

Several compromise, or combination, theories have been suggested. For example, J. J. Thomson[1] proposed what has since come to be called the "ether string" theory, according to which, radiation, leaving the source, proceeds as a wave motion along certain localized lines or "ether strings," much as sound waves might proceed from a source of sound along speaking tubes instead of as spherical waves of even growing radii. According to this concept, a wave front of light, if sufficiently magnified, would appear as a group of bright specks—the cross-section of these stream lines in the ether—on a dark background, rather than as a continuously luminous surface. If it be assumed that energy is streaming along each string at exactly the same rate, then the number of such strings per square centimeter of wave front determines the intensity of the radiation. These strings, each equally intense, would "strike" only here and there an atom,

[1] *Proc. Cambridge Phil. Soc.*, vol. 14, p. 417 (1906).

and, when photoelectric emission takes place, each electron would be given the same quantity of energy. Thus, many of the observed facts of the photoelectric phenomenon could be accounted for. But the theory was too much of the *ad hoc* kind to be either convincing or fruitful in suggesting new researches, and it is now, *probably*, of historical interest only.

In short, the situation is about like this: On one side of an impenetrable barrier, or fence, is to be found a group of phenomena—such as interference, polarization, smaller velocity of light in optically denser bodies, and, indeed, the whole electromagnetic theory and its ramifications—according to which we should say, without the slightest doubt, that light *must be* a wave motion. On the other side of the fence is to be found another group—the photoelectric effect and other phenomena which we shall consider in subsequent chapters—according to which we should say, again without the slightest hesitation, if we did not know what was on the first side of the fence, that light *must be* corpuscular. Just as the discovery of polarization, in 1811, led to a radical modification of the wave theory—namely, the substitution of the concept of *transverse* for longitudinal vibrations —so, today, the discovery of some new experimental fact or phenomenon may lead to a fusion of the undulatory and the corpuscular theories in some quite unexpected way or, indeed, may result in an entirely new theory. However that may be, the concept of *wave motion*, as a *description* of certain of the phenomena of radiation, has become an indispensible and a very real part of modern physics. And, likewise, the concept of *quanta* of radiant energy, as a *description* of certain other phenomena of radiation, has become equally real and indispensible. Either concept is used at will whenever the particular phenomenon at hand happens to yield to discussion or treatment more readily in terms of one concept than of the other. Ample confirmation of this will be found in the following pages.

CHAPTER VII

THE ORIGIN OF THE QUANTUM THEORY

The quantum theory, first proposed by Planck, in 1900, arose out of the inability of the classical physics to explain the experimentally observed distribution of energy in the spectrum of a black body. We have seen, in Chap. VI, how, likewise, the older theories of radiation could not explain the experimentally observed facts of the photoelectric effect. In the present chapter, we shall first discuss certain observed phenomena of radiation which any theory must explain. We shall then attempt to show (1) just how far the problem of black-body radiation can be solved by classical methods based first upon thermodynamics and then upon statistical mechanics and (2) at precisely what point each of these classical methods failed and the introduction of the concept of radiation quanta seemed to offer the only solution to the problem.

1. Thermal Radiation.—It is a matter of common observation that bodies when heated emit radiant energy—or, more simply, radiation—the *quantity* and *quality* of which depend, for any given body, on the temperature of that body. Thus, the rate at which an incandescent lamp filament emits radiation increases rapidly with increase in the temperature of the filament; and the quality of the radiation, as observed visually, changes markedly as the temperature increases—the emitted light being "whiter" at higher temperatures. Radiation, the quantity and quality of which, emitted by any given body, depends *solely* on the temperature of that body, is called *thermal* radiation. It is a characteristic of thermal radiation that, when dispersed by a prism or other similar means, a *continuous* spectrum is formed.

In order that thermal radiation may become visually observable, it is necessary that the temperature of the radiator should be (about) 500 to 550°C. or above. But that bodies radiate at a much lower temperature is easily observed by the feeling of warmth experienced when holding near the skin a heated body, say an iron ball heated a comparatively few degrees above body

temperature. Indeed, as early as 1792, Prévost proposed his famous "theory of exchanges," which states that there is a *continuous* interchange of energy between bodies as a result of the reciprocal processes of radiation and absorption. Thus, if we have a system of bodies in an enclosure, all at uniform temperature, each body receives (*i.e.*, absorbs) from its surroundings as much energy as it radiates. According to this concept, which agrees well with observation, any given body would cease to emit *thermal* radiation only when its temperature has been reduced to absolute zero.

Thermal radiation is emitted, ordinarily, only by solids or liquids.

There are many types of radiation other than thermal radiation. Thus, gases and vapors, when suitably "excited," emit a *characteristic* radiation, which, when dispersed, results in a line, or discontinuous, spectrum, the wave length of the several lines being characteristic of the emitting substance. The excitation may result from thermal agitation, electric discharge, bombardment by electrons, or absorption of incident radiation of suitable wave length. As examples may be mentioned the sodium flame, the mercury arc, and the luminescence of sodium vapor when illuminated by light of the *D* lines.

Characteristic radiation, in the X-ray region of the spectrum, is emitted also by solids and liquids when bombarded by electrons of suitable speeds. Such bombardment results, in addition, in the emission of a *continuous* X-ray spectrum.

Certain solids and liquids emit a characteristic radiation when illuminated (or excited) by light of suitable wave length, even though the intensity of the incident light is not sufficient to produce a perceptible rise of temperature of the emittor. This phenomenon is called *fluorescence* if the emission ceases as soon as the exciting light is removed and *phosphorescence* if the emission persists an apprecible time after removing the excitation. There is no sharp dividing line between fluorescence and phosphorescence. In general, the exciting light must be of shorter wave length than the fluorescent (or phosphorescent) radiation.[1]

Radiation of very high frequency, known as "gamma rays," is emitted during the process of the radioactive disintegration of the heavier elements.

[1] For a description of the phenomena of fluorescence and phosphorescence, see R. W. WOOD: "Physical Optics."

The classification of radiation into the several types—thermal, characteristic, fluorescent, etc.—is based, of course, upon superficial peculiarities in laboratory methods of production and study, rather than upon any *real differences* in the nature of the ultimate emitting mechanisms involved in the several cases. What these differences are, *if any*, we are not now in a position to state. As a matter of fact, considerable progress in the study of the problems of radiation can be made without inquiring either into the atomic mechanism involved or into the nature of radiation itself. Indeed, in this chapter, we shall see that *the classical methods were generally successful in discussions of thermal radiation which did not involve assumptions as to the nature of light* but which were, rather, concerned with certain *energy* relations. We have had occasion to point out a similar case in connection with Carnot's cycle, which was found to be correct irrespective of the particular theory of heat adopted.

2. Some Fundamental Concepts and Definitions. (*a*) *Total Emissive Power.*—The rate at which a given body emits radiation[1] depends upon the temperature of the body and on the nature of its *surface*. We may define the *total emissive power*, symbol E_s, of a body S as the "total radiant energy emitted per unit time per unit area of surface of the radiating body." The total emissive power E_s increases rapidly with increasing temperatures and may be conveniently expressed in ergs per square centimeter per second. Thus, the total emissive power of cast iron at a temperature of 1600°K.[2] is about 1.1×10^8 ergs per square centimeter per second; that of tungsten at 2450°K. is about 5×10^8 ergs per square centimeter per second (or 50 watts per square centimeter).

(*b*) *Monochromatic Emissive Power.*—If the radiation from a heated body, such as an incandescent lamp filament at a given temperature, be dispersed into a spectrum by a prism or other suitable device, it will be found, by means of a sensitive thermopile, that the energy in the spectrum is distributed among the various wave lengths in a regular manner, as is shown by the curve in Fig. 42, which shows the distribution of energy in the spectrum of tungsten at a temperature of 2450°K. We may define the *monochromatic emissive power*, e_λ, at any given wave length λ,

[1] In this chapter, unless otherwise stated, we shall use the term "radiation" to refer to *thermal* radiation, the adjective being omitted to save repetition.

[2] "K" refers to the absolute Kelvin scale of temperature, in centigrade degrees.

by saying that the radiant energy emitted in the spectral range λ to $\lambda + d\lambda$, per unit area per unit time, is given by $e_\lambda d\lambda$. Thus, the ordinates of the curve in Fig. 42 are e_λ, and the area of the shaded strip is $e_\lambda d\lambda$. Since the total emissive power E_s refers to *all* wave lengths combined, we obviously have the relation between E_s and e_λ given by

$$E_s = \int_0^\infty e_\lambda d\lambda \qquad (1)$$

That is, the total emissive power is proportional to the area between the curve and the wave-length axis. We shall consider in detail, later, the way in which E_s and e_λ vary with temperature.

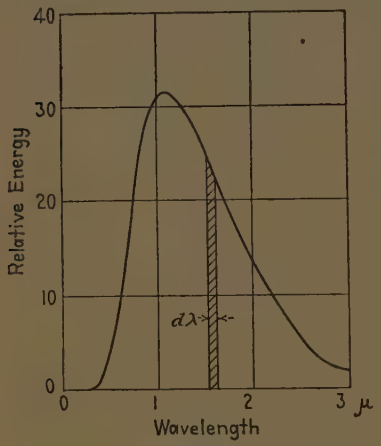

FIG. 42.—Distribution of energy in the spectrum of a tungsten lamp.

The terms "total emissive power" and "monochromatic emissive power" are not to be confused, respectively, with

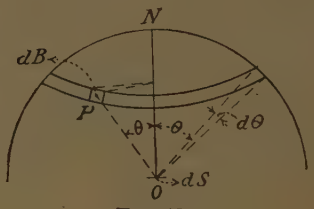

FIG. 43.

"total emissivity" and "monochromatic emissivity," which we shall define later (Sec. 4).

(*c*) *Intensity of Radiation from a Surface.*—It will be convenient, to avoid confusion, to define the term *intensity of radiation* from a surface. Let dS (Fig. 43) be a small surface element of a radiating body. Describe about dS a hemisphere of radius ρ, and let dB, located at P, be a small element of the surface of this hemisphere, the radius OP to this element making an angle θ with the radius ON which is normal to dS. The rate dQ/dt at which radiant energy is incident upon dB is easily seen to be proportional to (1) the area dB; (2) the apparent area[1] $dS \cos\theta$ of

[1] This is equivalent to saying that the rate at which a surface radiates energy in a direction θ from the normal to the surface is proportional to the cosine of θ. This well-known "cosine law" is obeyed only approximately, the deviations from the law being greater for large values of θ.

the radiator, as seen from P; (3) $1/\rho^2$, on account of the inverse-square law; and (4) to a quantity i_s which depends upon the temperature and character of the radiator, and which is called the *intensity of the radiation* of dS. That is, by proper choice of units,

$$\frac{dQ}{dt} = i_s dS \cos\theta \cdot \frac{dB}{\rho^2} \tag{2}$$

But dB/ρ^2 is the solid angle, call it $d\phi$, which the area dB subtends at O. For purposes of defining i_s we may, therefore, write

$$i_s = \frac{dQ/dt}{dS \cdot d\phi \cdot \cos\theta} \tag{3}$$

Or, in words, *the intensity of radiation i_s from the surface dS at any given temperature is equal to the rate at which dS radiates energy per unit of (its) area per unit solid angle in a direction normal to its surface* (*i.e.*, for $\cos\theta = 1$). This definition applies to the *total* radiation from the surface. Just as in the case of emissive power, we may designate by "monochromatic intensity of radiation," symbol i_λ, the intensity of radiation in a wave-length range $d\lambda$ at wave length λ.

There is a very simple relation between the total emissive power E_s and the intensity of radiation i_s. Referring to Fig. 43, if we assume (1) that the radiation from the surface dS is perfectly symmetrical about the normal ON and (2) that the surface obeys the cosine law, we may choose as an element of area of the hemisphere a ring of width $\rho d\theta$ and of length $2\pi\rho \sin\theta$ the area of the ring being, thus, $2\pi\rho \sin\theta \cdot \rho d\theta$. The flux of energy dQ/dt through this ring is given, as in equation (2), by

$$\frac{dQ}{dt} = i_s\, dS \cos\theta \cdot \frac{2\pi\rho(\sin\theta) \cdot \rho d\theta}{\rho^2} \tag{4a}$$

$$= 2\pi i_s dS \cos\theta \sin\theta\, d\theta \tag{4b}$$

If this equation be integrated from $\theta = 0$ to $\theta = \pi/2$, we shall have the total rate of flux of energy dQ/dt from dS. We have designated by E_s the rate of flux of energy per unit area from a surface. Therefore,

$$E_s = \frac{dQ/dt}{dS} = 2\pi i_s \int_0^{\pi/2} \cos\theta \sin\theta\, d\theta$$

$$= \pi i_s \sin^2\theta \Big]_0^{\pi/2} \tag{5}$$

$$\therefore E_s = \pi i_s \tag{6}$$

And, similarly, we have

$$e_\lambda = \pi i_\lambda \tag{7}$$

(*d*) *Absorptivity.*—In general, radiation, falling upon a surface, is partly absorbed, partly reflected, and, unless the body be very thick or very opaque, partly transmitted. We shall define the *absorptivity* of a surface, symbol A, as the fraction of the radiant energy, incident on the surface, which is absorbed. Absorptivity is (1) a pure numeric; (2) for any actual body, less than unity; and (3) varies greatly with wave length of the incident radiation and, to a lesser extent, with the temperature of the absorber.

As we shall see in Sec. 4, there is a very simple relation between the total emissive power E_s of a surface and its absorptivity A.

(*e*) *Reflectivity.*—We may define the reflectivity of a surface, symbol R, as the fraction of the radiant energy incident upon the surface, which is reflected. R is a pure numeric.

(*f*) *Transmissivity.*—Likewise, we may define the transmissivity, symbol T, of a body as the fraction of the radiant energy, incident on the surface of the body, which is transmitted. We shall, in this chapter, confine our attention to cases where the body is so thick or so opaque as to transmit no energy, *i.e.*, to bodies for which $T = 0$. In these cases, since all the incident radiation is, then, either reflected or absorbed, we may write

$$A + R = 1 \tag{8}$$

(*g*) *The Density of Radiation.*—The radiant energy per unit volume in a stream of radiation is spoken of as the "energy density of the radiation," symbol ψ. Thus, the solar constant[1] is about 1.3×10^6 ergs per square centimeter per second. This is the amount of energy contained in a column[2] of solar radiation 1 sq. cm. in cross-section and 3×10^{10} cm. long, *i.e.*, in 3×10^{10} cc. The energy density ψ_s of the sun's radiation in the neighborhood of the earth is, therefore,

$$\psi_s = \frac{1.3 \times 10^6}{3 \times 10^{10}} = 4.3 \times 10^{-5} \text{ ergs per cubic centimeter}$$

In the case of the sun's rays, just considered, the radiation is streaming in parallel directions. A different condition exists in the interior of a hollow heated enclosure. Here radiation is streaming back and forth in all possible directions. And the term "energy density" then refers to the total quantity ψ of this

[1] The solar constant is the amount of the sun's radiation received on unit area in unit time, the receiving area being perpendicular to the sun's rays and at a distance from the sun equal to the mean radius of the earth's orbit.

[2] The column being chosen in the neighborhood of the earth's orbit, and the sun's rays being considered parallel throughout the length of the column.

radiation in unit volume of the interior. Assuming symmetrical, equilibrium conditions within the interior, we may, for simplicity, regard this radiation the same *as if* an amount $\psi/3$ were streaming in parallel streams in *each* of three mutually perpendicular directions.

3. The "Black Body" and Its Properties.—We have, in nature, no bodies which absorb all the radiation falling upon them, *i.e.*, we have no bodies for which the absorptivity is one. Some bodies, however, such as black velvet or lampblack, reflect only a very small fraction of the incident radiation, and in common parlance we speak of such bodies as "black." Borrowing the term for scientific phraseology, we may define the *perfect* or *ideal black body* as a body the surface of which absorbs all the radiant energy incident upon it. For such a body, $A = 1$ and $R = 0$.

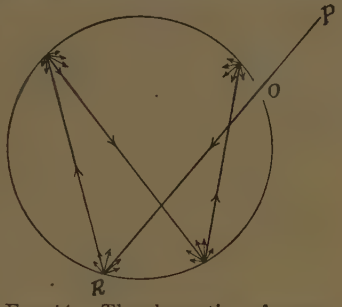

FIG. 44.—The absorption of energy by a black body.

Although no such body actually exists, we may approximate it as closely as we please for both theoretical and experimental purposes by making use of a small hole in the side of a hollow enclosure. Thus, in Fig. 44, let a ray of radiant energy PR enter the small hole O in the side of a hollow sphere, say of iron. A large part of the radiation is absorbed as it strikes the inside of the sphere at R, the remainder being *diffusely* reflected. Only a very small fraction of this diffusely reflected energy goes out through the hole, the rest being finally completely absorbed by successive reflections. Theoretically, perfect absorption would be reached only when the area of the hole is infinitely small compared to the area of the hollow interior. Practically, an approximation sufficient for experimental purposes is obtained by using a hole 1 or 2 cm. in diameter in the end of a hollow cylindrical tube some 20 cm. long and 4 or 5 cm. in diameter.

When such an enclosure is heated, the inside walls radiate, and some of this radiation passes out through the hole. That is to say, *the "black body" may radiate, as well as absorb, energy.* Such radiation is called "black body" radiation. Its properties are of great importance, for both theoretical and experimental purposes, in studying the phenomena of radiation. We shall

designate by E (without subscript) the *total* emissive power of the black body. As we shall see in Sec. 5 of this chapter, E depends only on the temperature, and not on the material, of the hollow enclosure.

4. Relation between Absorptivity and Emissive Power.—In 1833, Ritchie[1] performed an experiment which is very instructive in connection with theories of radiation. A and B (Fig. 45), are two hollow cubes containing air and connected by a glass tube TT, in which is a small drop of fluid I to serve as an index, the combination forming a differential air thermometer. Between A and B is placed a third cubical vessel C, which may be filled with hot water. The faces *2*, *2* of B and C, respectively, are covered with a thin coating of lampblack. The faces *1*, *1* of A and C, respectively, are of, say, silver and are highly polished. The position of the index I is noted, and then hot water is poured into C. Whereupon, the compartments A and B are heated by radiation from C. B is heated by virtue of the fact that its surface *2* absorbs a certain fraction of the energy radiated by surface *1* of C; and *vice versa* for A. Since the respective emitting and absorbing surfaces are inverted for the two compartments, it might be expected, on account of this dissymmetry, that one of the compartments would absorb heat at a greater rate than the other. But on performing the experiment, *it is observed that the index I does not move when C is filled with the hot water. A and B each absorb energy at the same rate.* This experiment leads to a law of extraordinary importance, which may be derived as follows:

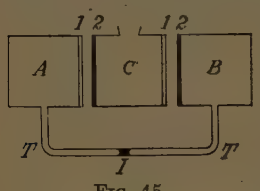

FIG. 45.

Let E_1 and A_1 represent, respectively, the total emissive power and the absorptivity of surface *1*; and E_2 and A_2, the corresponding quantities for surface *2*. Assuming the emitting and absorbing faces each to have unit area, the rate of emission from C toward B is given by E_1. A fraction A_2 of this energy, is absorbed by surface *2* and enters B. That is, B is receiving energy at a rate A_2E_1. Similarly, A is receiving energy at a rate A_1E_2. Now, Ritchie's experiment shows that these two rates are equal. Therefore,

$$A_2E_1 = A_1E_2$$

[1] *Ann. der Physik und Chemie*, vol. 28 (Poggendorf), p. 378 (1833).

or,

$$\frac{E_1}{A_1} = \frac{E_2}{A_2} \qquad (9)$$

In this same manner, we may compare other surfaces—*3*, *4*, *5* . . —in turn with surface *1*, and we may include, in this comparison, *a black body* the emissive power of which we designate by E and the absorptivity of which is unity. We may, then, write,

$$\frac{E_1}{A_1} = \frac{E_2}{A_2} = \frac{E_3}{A_3} = \cdots = \frac{E}{1} = E \qquad (10)$$

In words: *At a given temperature, the quotient obtained by dividing the emissive power by the absorptivity of any body is the same for all bodies and is equal to the emissive power of a black body at the same temperature.* This is known as *Kirchhoff's law*, derived by Kirchhoff, in 1859.

The derivation of Kirchhoff's law on the basis of Ritchie's experiment is open to several objections among which is the fact that the two surfaces of the same kind (*i.e.*, the two lampblack surfaces, for example) are not at the same temperature. An alternative derivation which avoids this difficulty is as follows: Consider a uniformly heated enclosure (Fig. 46), say the inside of a hollow iron sphere, in which are two *very small* spherical bodies B_1 and B_2 of respective superficial areas S_1 and S_2.

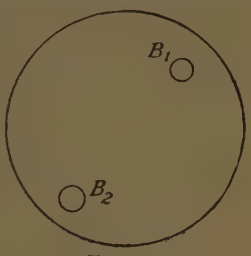

FIG. 46.

After a time, these bodies will reach the same temperature as that of the interior, and, thereafter, each will radiate as much energy as it absorbs. (We assume the interior of the sphere to be evacuated, so as to avoid convection currents.) Within the enclosure, radiation will be streaming uniformly in all directions, and there will fall upon the two bodies in unit time exactly the same incident radiation *per unit area*, call it I. Let E_1, A_1 and E_2, A_2 be the respective emissive powers and absorptivities of the two bodies. Then B_1 will emit radiation at a rate E_1S_1 and will absorb radiation at a rate A_1IS_1. Since the temperature of B_1 remains constant, we have

$$E_1S_1 = A_1IS_1$$

And for body B_2, we have, similarly,

$$E_2S_2 = A_2IS_2$$

From these two equations, we at once obtain, as before,

$$\frac{E_1}{A_1} = \frac{E_2}{A_2} \tag{9}$$

The same argument could be extended to any number of bodies within the enclosure.

A similar, though somewhat more rigorous, discussion would show that Kirchhoff's law applies to the ratio of the monochromatic emissive power e_λ to the monochromatic absorptivity A_λ at the same wave length. That is,

$$\frac{e_\lambda}{A_\lambda} = \text{constant} \tag{11}$$

the constant being the monochromatic emissive power of a black body at the same temperature.

Note.—There is considerable confusion in the terminology of the emission and absorption of radiation. Thus, for the quantity which we have herein defined as "total emissive power," one finds used, variously, such terms as "radiating power," "emission," and "emissivity." And for the quantity which we have called "absorptivity,"[1] one finds "absorbing power" and "absorptive power." The use of the word "power" in "total emissive *power*" is obviously justified. For, "power" in the technical sense, in physics and engineering, means a "rate of doing work" or of delivering energy; and a radiating surface is emitting energy at a definite rate. But "power" used in connection with absorption, as in the term "absorbing *power*," is clearly an incorrect use of the word; for the quantity *defined* does not involve a *rate* of absorbing energy.

One must distinguish between "absorptivity," as herein defined, and "coefficient of absorption," which latter is an entirely different term, referring to the absorption of radiation in its passage *through* matter. Thus, if a beam of radiation of intensity I_0 is incident upon and passes through a slab of absorbing material (such as light through smoked glass), the thickness of which is d, the intensity I of the emerging beam is given by the equation $I = I_0 e^{-\mu d}$, where "e" is the Naperian base of logarithms and μ is the *coefficient of absorption* of the material.

It is essential, also, to distinguish between the terms "total emissive power" and "emissivity." If E_1 is the total emissive power of a body at temperature T, and E is the total emissive power of a black body at the same temperature, we have seen (equation (10)) that

$$\frac{E_1}{A_1} = E$$

where A_1 is the absorptivity of the substance. Now, the emissivity of a surface is defined as "the ratio of *its* total emissive power to the total emis-

[1] So far as possible, the terminology defined in the International Critical Tables, vol. 1, pp. 34–42, has been adopted in this chapter.

sive power of a black body at the same temperature;" *i.e.*, emissivity equals E_1/E. It is, thus, seen that the emissivity of a substance is a pure numeric and is equal to its absorptivity. The same relations hold between monochromatic emissive power and the corresponding absorptivity.

One or two comments may be made in passing: No body can emit (*thermal*) radiation at a greater rate than can a black body at the same temperature. For, the quotient E_S/A_S is constant for all bodies, including the black body. The value of A for the black body is the maximum possible, namely unity. Therefore the emissive power of a black body is also the maximum possible. For this reason, since the black body is called a *perfect* absorber, it may, also, be called a *perfect* radiator.

Actual bodies are inferior, as radiators, to the experimental black body. Thus, tungsten, at 2750°K., radiates, per unit area, only about 25 per cent as much energy as a black body at the same temperature. For iron at 1600°K., the corresponding fraction is about 30 per cent.

5. The Emissive Power of a Black Body.—It will be instructive to examine a little more closely the factors which determine the rate of emission of energy from a black body. Equal areas of actual bodies—silver, tungsten, carbon, iron—maintained at the same temperature will emit quite different amounts of energy. That is to say, the radiation from an actual body depends both on the nature of the body and on its temperature. Is the radiation from a black body, likewise, dependent both on the temperature and the material of the hollow enclosure, the hole in the side of which forms the black body?

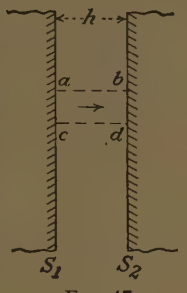

FIG. 47.

To simplify the discussion of this question, of course at the expense of generality, consider the two dissimilar but parallel surfaces S_1 and S_2, which form the opposite faces of a flat, disk-shaped enclosure, the distance h between S_1 and S_2 being small compared to their lateral dimensions. Sections of these surfaces are shown in Fig. 47. Let the exterior faces of the enclosure be impervious to heat, and let the temperature within the enclosure have reached a constant value T. Each surface is then emitting as much as it absorbs. Although, actually, radiation is streaming in every direction within the enclosure, on account of the small distance between the faces S_1 and S_2 compared to their

dimensions, we may consider the phenomenon the same *as if* all the radiation were streaming back and forth at right angles to the two surfaces. Let E_1, A_1 and E_2, A_2 be the respective total emissive powers and absorptivities of the two surfaces. Further, we shall assume that the radiation travels with the velocity of light c.

Consider, now, the "history" of the radiation emitted by unit area (1 sq. cm.) of S_1 during a time dt just sufficient for the radiation, streaming toward S_2, to fill a column 1 sq. cm. in cross-section and of length h equal to the distance between the surfaces. The amount of this radiation contained in the column is $E_1 dt$, the relation between h and dt being given by

$$h = c\,dt \tag{12}$$

This energy falls upon S_2, where a fraction A_2 is absorbed and the remaining fraction $(1 - A_2)$ is reflected. After reflection from S_2 we shall have a column streaming toward S_1, and the energy contained in this column will be $E_1(1 - A_2)dt$. After this, in turn, has been reflected from A_1 and is streaming toward the right again, we shall have $E_1(1 - A_1)(1 - A_2)dt$. And so on, for successive reflections. These successive values, together with arrows representing the respective directions in which the radiation is moving, are shown in column 1 of the following table:

RADIATION INITIALLY EMITTED BY S_1	RADIATION INITIALLY EMITTED BY S_2
	$\leftarrow E_2 dt$
$\rightarrow E_1 dt$	$\rightarrow E_2(1 - A_1)dt$
$\leftarrow E_1(1 - A_2)dt$	$\leftarrow E_2(1 - A_1)(1 - A_2)dt$
$\rightarrow E_1(1 - A_1)(1 - A_2)dt$	$\rightarrow E_2(1 - A_1)^2(1 - A_2)dt$
$\leftarrow E_1(1 - A_1)(1 - A_2)^2 dt$	$\leftarrow E_2(1 - A_1)^2(1 - A_2)^2 dt$
$\rightarrow E_1(1 - A_1)^2(1 - A_2)^2$	$\rightarrow E_2(1 - A_1)^3(1 - A_2)^2 dt$
etc.	etc.

In column 2 are shown values, after successive reflections, of energy $E_2 dt$, initially emitted by S_2 during the *same* time interval dt.

It is easy to see that, when a steady state has been reached, there exist simultaneously columns of radiation, streaming right and left, as shown in the table. Suppose we now wish to compute the radiation W_r which, at any given instant, is streaming toward the right. We should simply have to add those terms in the above table with arrows pointing toward the right.

That is,

$$W_r = [E_1 dt + E_1(1 - A_1)(1 - A_2)dt + E_1(1 - A_1)^2(1 - A_2)^2 dt + \ldots] + [E_2(1 - A_1)dt + E_2(1 - A_1)^2(1 - A_2)dt + E_2(1 - A_1)^3(1 - A_2)^2 dt + \ldots] \quad (13)$$

This readily reduces to[1]

$$W_r = \frac{E_1 + E_2(1 - A_1)}{A_1 + A_2 - A_1 A_2} dt \quad (14)$$

By Kirchhoff's law (equation (9)),

$$E_2 = \frac{A_2}{A_1} E_1$$

Putting this value of E_2 in equation (14), we readily find, after simplifying,

$$W_r = \frac{E_1}{A_1} dt = E dt \quad (15)$$

where, as before, $E\ (= E_1/A_1)$ is the total emissive power of a black body. That is to say, *the radiant energy streaming to the right within a column* $h = cdt$ *cm. long and* 1 *sq. cm. cross-section is* Edt, or E/c units of energy per cubic centimeter.

If, now, a small hole, say of unit area, be opened up in the right-hand face, this radiation, streaming toward the right opposite the hole will pass out through the hole, the density of the radiation, *i.e.*, the radiant energy per unit volume emerging from the hole, being E/c; or, in 1 unit of time an amount of energy equal to E per unit area will be "emitted" by the hole. We thus see (1) *that a hole in the side of the hollow, heated enclosure emits radiation as if the hole were a perfect black body* and (2) *that this rate of emission is quite independent of the nature of the interior surfaces.*

Thus, as previously pointed out, a hole in the side of a hollow enclosure not only *absorbs* as if it were a perfect black body, but it also emits radiation at the same rate as would a perfect black body. Since this rate E is independent of the *material* of the enclosure, it can depend only on the *temperature* T of the enclosure; *i.e.*, E is some function of T, or,

$$E = f(T) \quad (16)$$

[1] *Hint:* These sums are of the form $1 + x + x^2 + \ldots$, where $x = (1 - A_1)(1 - A_2)$. Since both A_1, and A_2 are always positive and less than unity, $0 < x < 1$, and $1 + x + x^2 + \ldots = 1/(1 - x)$.

It was one of the important successes of classical physics to find the exact form of this function. As we shall see in subsequent sections, the solution of this problem was reached *without the necessity of making any postulates as to the nature of radiant energy.*

6. Pressure of Radiation.—That radiation falling upon a body exerts a pressure in the direction of motion of the radiation is by no means a concept peculiar to modern physics. Over 300 years ago, Kepler suggested that the curvature of comets' tails away from the sun might be due to light pressure. Newton recognized that Kepler's suggestion was in harmony with the corpuscular theory of light.[1] And later, Euler showed that such a pressure should follow on the wave theory of light.

Experimentally, the subject was attacked by Du Fay, about 1750; by Bennet, in 1792; by Fresnel, in 1825; by Crookes, in 1873; and by Zöllner, in 1877—all with inconclusive or conflicting results, due for the most part to the disturbing action of the gas surrounding the illuminated surface.

Meanwhile, Maxwell, in 1871, proved conclusively that a radiation pressure is to be expected on the basis of the electromagnetic theory of light. Qualitatively, the line of argument is somewhat as follows: (1) Lines of either electric or magnetic force may be thought of as being under stress longitudinally and as repelling each other laterally, this repulsion causing a *lateral pressure* in the field. (2) According to the electromagnetic theory, light consists of electric and magnetic vibrations *at right angles* to the directions of propagations of the light. The lateral pressure in these vibrating electric and magnetic fields is, therefore, *parallel to* the direction of propagation of the light. (3) When electromagnetic radiation is absorbed by a surface, these fields are destroyed at the surface and the lateral pressure of the fields in the oncoming waves produces a pressure on the surface.

Quantitatively, it may be shown[2] that the lateral pressure in an electric field F or in a magnetic field H is, respectively, $F^2/8\pi$ or $H^2/8\pi$. When a train of electromagnetic waves falls *normally* onto a surface, both the electric field and the magnetic field cause periodically varying pressures on the surface, the *average* values of the pressure being $F_0^2/16\pi$ and $H_0^2/16\pi$, where F_0 and H_0 are the

[1] Just as the pressure produced by a gas is due to the impact of its molecules.

[2] See any treatise on electricity and magnetism, such as STARLING: "Electricity and Magnetism."

respective maximum values of the two vectors. (We assume, for simplicity, a plane-polarized wave.) The average value of the *total* pressure onto the surface is the sum of these two. But it has been shown (Chap. IV, Sec. 8) that the average energy per unit volume in an electromagnetic wave train is $F_0^2/16\pi + H_0^2/16\pi$, which is identical with the expression for the pressure. Therefore, the very far-reaching conclusion: *The pressure p exerted by radiation onto a perfectly absorbing surface is numerically equal to the energy per unit volume in the beam of radiation incident onto the surface.* This latter quantity we have called (see Sec. 2(g), this chapter) the "radiation density" ψ. Accordingly, for a *parallel* beam of radiation incident *normally* onto a perfectly absorbing surface, we have

$$p = \psi \tag{17}$$

If we are dealing with the radiation of density ψ in a uniformly heated enclosure, such as, for simplicity, a hollow cube in which radiation is incident onto the inner surfaces at all possible angles from 0 to $\pi/2$, we may conclude, from the fact that the pressures on the three pairs of opposite faces must be equal, that the radiation may be thought of as divided into three equal parallel beams each of density $\frac{1}{3}\psi$, each beam being reflected back and forth normally between a pair of parallel faces. In this case, the pressure on each face would be $\frac{1}{3}\psi$, where ψ is the *total* radiation density within the enclosure. That is, the pressure p produced on the walls of a hollow heated enclosure, by the radiation within the enclosure, is, for an enclosure of any form, given by

$$p = \tfrac{1}{3}\psi \tag{18}$$

where ψ is the actual density of the radiation.

It can be shown that the pressure due to radiation is a consequence of the law of the conservation of energy and is, therefore, independent of, or more fundamental than, any theory of radiation. Thus, consider a parallel stream of radiation, of density ψ, falling normally onto a black body of unit area (1 sq. cm.). Energy is entering the body at a rate $c \cdot \psi$, where c is the velocity of light. Now let the black body be displaced a distance h opposite to the direction of the incident radiation. As a result of this displacement more energy will have entered the black body than would have entered had the body remained stationary, by the amount of the radiation contained in a column of the incident stream 1 sq. cm. in cross-section and h cm. long, *i.e.*, by the

additional amount of energy $h\psi$. To introduce this additional energy into the black body requires that a force f shall have acted on the body to produce the displacement h such that the work $f \cdot h$ done by the force shall equal ψh. This force f must be balanced by an opposing force by which the radiation must act on the black body; and, since the black body has unit area, this force f is numerically equal to the *pressure* p of the radiation. That is,

$$p \cdot h = \psi h$$

or

$$p = \psi \tag{19}$$

in agreement with equation (17). In this derivation of equation (19), nothing was said about the nature of radiant energy.

If the radiation is totally reflected, instead of totally absorbed, the energy density in front of the reflector is doubled, and the pressure on the reflector is, therefore, double that which would be experienced by a black body which has the same incident radiation.

Under ordinary terrestrial conditions, this pressure p due to radiation is a very small quantity. For example, as pointed out in Sec. 2(g) of this chapter, the energy density of solar radiation incident upon the earth is 4.3×10^{-5} ergs per cubic centimeter. Accordingly, the pressure which the sun's radiation exerts on the earth's surface normal to the direction of the rays is 4.3×10^{-5} dynes per square centimeter. It is, therefore, not to be wondered at that Drude, as late as 1900,[1] remarked that "this pressure . . . is so small that it cannot be detected experimentally." Nevertheless, almost simultaneous with Drude's statement came the announcements of two independent researches—one in Europe, by Lebedew,[2] and the other in America, by Nichols and Hull[3]—in which the pressure due to radiation *was* actually measured with acceptable precision and the measured value was found to agree almost perfectly with that predicted by theory!

For an account of this extremely important investigation the reader is referred to the complete paper by Nichols and Hull,[4] who

[1] DRUDE: "Theory of Optics" (English translation by Mann and Millikan), p. 491.

[2] *Rapports présentes au Congrès International de Physique*, Paris, 1900.

[3] *Science* (October, 1901).

[4] *Phys. Rev.*, vol. XVII (First Series), pp. 26 and 91 (July and August, 1903).

measured the intensity of a beam of radiation by allowing it to fall onto a blackened silver disk of known mass, the rate of rise of temperature of the disk being observed. This same beam was then allowed to fall onto a mirror system comprising a torsion balance suspended by a quartz fiber in an evacuated enclosure, the deflection produced by the radiation being observed. Knowing the constants of the torsion balance, it was possible to compute the pressure produced by the radiation. The agreement between theory and experiment for three different beams of radiation is shown by the following table taken from the paper by Nichols and Hull:

Beam filtered through	Observed pressure, dynes per square centimeter	Observed energy densities, ergs per cubic centimeter
Air	7.01×10^{-5}	7.05×10^{-5}
Red glass	6.94	6.86
Water cell	6.52	6.48

The agreement is seen to be excellent.

The experimental demonstration of the existence of radiation pressure points to a very fundamental similarity which exists between radiation and a perfect gas. A gas confined within an enclosure, at a given temperature, consists of molecules moving in all possible directions with an average velocity dependent on the temperature. By virtue of the kinetic energy of these molecules, each unit volume of the gas contains a definite amount of energy, which is determined by the temperature. These molecules impinge on and rebound from the walls of the containing vessel at all angles of incidence from 0 to $\pi/2$, producing thereby a pressure which depends on the temperature of the gas. This pressure is independent of the nature of the walls of the container. Likewise, if we have a hollow enclosure completely empty of all gas and at a definite temperature, there will be radiation streaming back and forth in all directions. Irrespective of whether radiation be corpuscular or undulatory, each unit volume of the enclosure contains a definite amount of energy ψ which is determined by the temperature.[1] This radiation is incident onto the

[1] In the case of the gas, the energy per unit volume is determined by the *velocity* (linear and angular) of the molecules. In the case of radiation, the *velocity* of the radiation remains fixed independent of temperature. On

walls of the enclosure at all angles from 0 to $\pi/2$. Part of the radiation is reflected, and part is absorbed and reemitted, the whole process producing a pressure which depends on the temperature and is independent of the nature of the enclosing walls. This similarity between radiation and a perfect gas makes it possible to apply to radiation the laws and methods of thermodynamics, such as are applied, with far-reaching results, to gases. In the next section, we shall discuss the application of Carnot's cycle to the problem of determining the relation between the emissive power of a black body and its temperature, using the concept of radiation pressure as just discussed.

7. The Stefan-Boltzmann Law.—(*a*) In 1879, Stefan,[1] on the basis of data observed by Tyndall, was led to suggest that the total emissive power of any body is proportional to the fourth power of its absolute temperature. Tyndall had shown that the ratio of the radiation from a platinum wire at 1200°C. to the radiation from the same wire at 525°C. was as 11.7:1. Stefan pointed out that the ratio

$$\frac{(1{,}200 + 273)^4}{(525 + 273)^4} = 11.6$$

thus indicating that

$$E_{Pt} = \sigma_{Pt} \cdot T^4 \tag{20}$$

where E_{Pt} is the emissive power of the platinum at absolute temperature T and σ_{Pt} is some constant. Subsequently, Boltzmann[2] deduced the same law from theoretical considerations by applying the laws of Carnot's cycle to the radiation in an "ether engine," the radiation playing the part of the working substance.

The ideal Carnot engine consists of a cylinder with walls impervious to heat; a piston likewise impervious to heat and moving without friction; and a base (end opposite to piston) which is a perfect (thermal) conductor. It may assist the reader to call

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the corpuscular theory, the increase in energy with temperature comes from an increase in the *number* of corpuscles. On the undulatory theory, the increase comes from an increase in the amplitude of the light vector. In the case of the gas, we have a distribution of velocities (more correctly, of energies) among the molecules, a particular velocity being the most probable. In the case of radiation, we have a distribution of energy among the various frequencies, a particular frequency possessing a maximum energy.

[1] *Wien Akad. Sitzungsberichte*, vol. 79, p. 391 (1879).

[2] *Wiedemann's Annalen*, vol. 22, pp. 31, 291 (1884).

attention to the usual cycle of events, in the case where an ideal gas is used as a working substance:

(*a*) Initially, the cylinder, containing a volume v_1 of perfect gas at a pressure p_1 and a temperature T_1, is placed with its perfectly conducting base on a source of heat at a temperature T_1, as shown at (*a*) in Fig. 48. The initial position of the piston is indicated at P_1 corresponding to the state of the gas p_1, v_1, T_1. The gas is allowed to expand *slowly*, pushing the piston upward until the pressure and volume are p_2 and v_2. The cooling which the gas would experience as a result of doing work against the external pressure is prevented by the conduction of

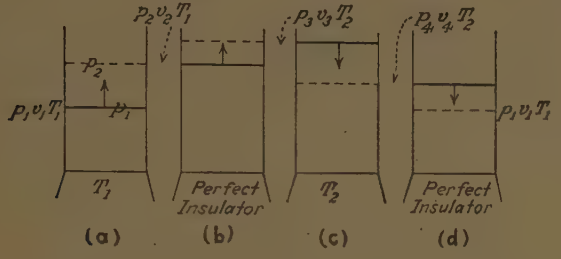

FIG. 48.—Carnot's engine.

heat, in total amount H_1, through the perfectly conducting base from the heat reservoir at temperature T_1. The expansion takes place so slowly that the temperature of the gas remains constant during the expansion and the process is said to be an *isothermal* process. It is represented on the p-v (pressure-volume) diagram, in Fig. 49, by the line between the points P_1 and P_2.

(*b*) The cylinder is then transferred to the perfect insulating stand, as shown in (*b*) (Fig. 48), and further expansion is allowed to take place until the pressure and volume are p_3 and v_3, respectively. Since no heat is allowed to enter during this process, the external work done by virtue of the expansion must cause a drop in temperature of the gas to temperature T_2. This process is an adiabatic process and is represented in Fig. 49 by the line between the points P_2 and P_3.

(*c*) The cylinder is now transferred to the heat "sink" at temperature T_2 (Fig. 48 (*c*)), and the gas is compressed slowly to volume v_4 and pressure p_4, the heat H_2, pro-

duced in the gas by the compression, flowing through the conducting base to the heat reservoir, and the temperature of the gas remaining constant. This is an isothermal process and is shown by the line between P_3 and P_4 of Fig. 49.

(p) Finally, the cylinder is again placed on the insulating stand (Fig. 48(d)), and the gas is further compressed, along an adiabatic, P_4P_1 of Fig. 49, until the initial pressure, volume and temperature are reached.

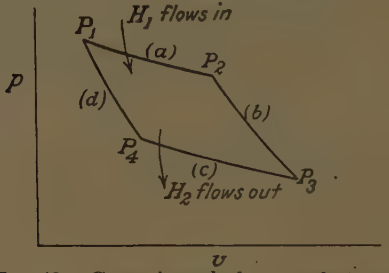

FIG. 49.—Carnot's cycle for a perfect gas.

We are concerned, in what follows in this article, chiefly with the efficiency of the cycle. This we may express either as[1]

$$\text{Efficiency} = \frac{\text{Area of cycle, } P_1P_2P_3P_4}{H_1}$$

or as

$$\text{Efficiency} = \frac{T_1 - T_2}{T_1}.$$

Therefore,

$$\frac{T_1 - T_2}{T_1} = \frac{\text{Area of cycle}}{H_1} \qquad (21)$$

If the adiabatic expansion, P_2 to P_3, is (relatively) very small, the temperature difference between the upper and lower isothermal is so small that we may write

$$T_1 - T_2 = dT$$

and under these restrictions, we may write equation (21)

$$\frac{dT}{T} = \frac{\text{Area of cycle}}{H_1} \qquad (22)$$

(b) The fundamental principles involved in using radiation as the working substance in the Carnot cycle differ in no way from the above. Only the details of the ideal operating mechanism are somewhat different from those employed in the case of

[1] For derivation, see any standard text.

the perfect gas engine. We may picture Boltzmann's "ether engine" as made up of a hollow cylinder and a frictionless piston. The entire cylinder walls, piston and base are impervious to heat; have vanishingly small heat capacity; and are placed in a perfect vacuum. In the base is a small opening O, serving as a black body, through which radiation may either enter or leave, and which may be covered at will by a perfectly reflecting cover impervious to heat. The cylinder, whatever its initial temperature, is placed with the opening O uncovered and opposite the black body B_1 which is *maintained* at a temperature T_1 (Fig. 50(a)). Radiation from B_1 enters the opening O, and, presently, the interior of the cylinder, *whatever the nature of its inner walls*,

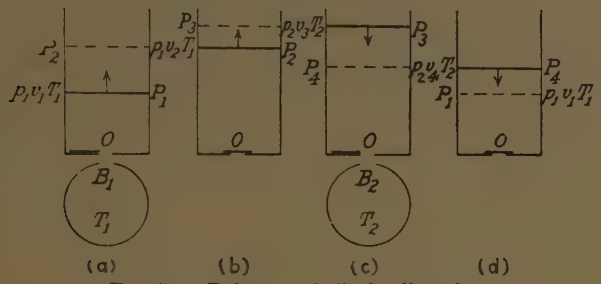

FIG. 50.—Boltzmann's "ether" engine.

reaches the temperature T_1, at which time the rate of radiation from O to B_1 is the same as the rate of radiation from B_1 to O. Under these conditions, the radiation density ψ within the cylinder has a certain definite value determined only by T_1. We require to find the general relation between ψ and T; for if we know ψ, the radiation *density* within the cylinder, we may, at once, determine the emissive power of the opening in the cylinder—*i.e.*, the emissive power of a black body—as explained in Sec. 5 of this chapter.

Remembering that when the energy density within the cylinder is ψ, the pressure on the cylinder walls of $\frac{1}{3}\psi$ (see equation (18)), we may now consider the following cycle of events:

(a) Starting with the piston in the initial position P_1, (Fig. 50(a))—the initial temperature being T_1; the initial volume v_1; and the initial pressure $p_1 = \frac{1}{3}\psi_1$—we allow the piston to move upward, *slowly*, as a result of the pressure, until position P_2 is reached, the volume increasing to v_2. If, during this process, the tempera-

ture within the cylinder is to remain constant at T_1, radiation in amount H_1 must enter the opening O from the black body B_1, for two reasons:

1. External work W_e is done by the piston. If T_1 remains constant, ψ_1 and, therefore, p_1 likewise remain constant, and

$$W_e = \tfrac{1}{3}\psi_1(v_2 - v_1) \tag{23}$$

2. The interior of the cylinder has *increased* in volume $(v_2 - v_1)$, which requires an additional influx of energy equal to $\psi_1(v_2 - v_1)$.

To maintain the temperature constant, the influx H_1 of radiation from B_1 must be given by

$$\begin{aligned} H_1 &= \tfrac{1}{3}\psi_1(v_2 - v_1) + \psi_1(v_2 - v_1) \\ &= \tfrac{4}{3}\psi_1(v_2 - v_1) \end{aligned} \tag{24}$$

This isothermal process is represented on the p-v diagram (Fig. 51) by the line P_1P_2. If we make the expansion during this isothermal process *very small*, we may write $(v_2 - v_1) = dv_1$, and the corresponding small amount of radiation dH flowing in to keep the temperature constant at T_1 is given by

$$dH_1 = \tfrac{4}{3}\psi_1 dv \tag{25}$$

(*b*) When the piston has reached P_2, the perfectly reflecting cover is placed over the opening O (Fig. 50(*b*)), thereby effecting complete thermal isolation of the interior of the cylinder, and a further expansion to position P_3 is allowed to take place. External work is done, as before, by the piston. The energy required for this external work must be supplied by the radiation within the cylinder. Partly because of this external work, partly because of the increase in volume during this process, *the energy density of the radiation within the cylinder must decrease* from ψ_1 to ψ_2, and, therefore, the temperature within the cylinder must decrease[1]

[1] That the temperature within the cylinder has decreased can be shown by again placing the engine, after the piston has reached P_3 in the position shown in Fig. 50(*a*), opposite the black body B_1. On removing the slide from the opening O, radiation will stream from O to B_1 at a lesser rate than at the beginning of process (*a*). Since B_1 is at the same temperature T_1 as formerly, more radiation will enter O than leaves. The temperature within the cylinder, therefore, will increase until the former temperature T_1 is reached and equilibrium between O and B_1 is again established.

from T_1 to T_2. The pressure, likewise, has decreased, since ψ has decreased. This is, obviously, an adiabatic process and is represented in Fig. 51 by the line P_2P_3.

If we make the expansion during this process *very* small, we may represent the change in temperature $(T_1 - T_2)$ by dT and the corresponding change in energy density $(\psi_1 - \psi_2)$ by $d\psi$. Since $p = \frac{1}{3}\psi$, we have

$$dp = \tfrac{1}{3}d\psi \qquad (26)$$

where dp represents the change in pressure during the process.

(*c*) The engine, now at the lower temperature T_2, is placed opposite the black body B_2 (Fig. 50(*c*)), at temperature T_2, the slide removed from the opening O, and the piston is moved, by the application of suitable external force, from P_3 to P_4. On account of this compression, there is a tendency for the temperature within the cylinder to rise and for the rate of emission of radiation from O to B_2 to increase. The compression is supposed to take place so slowly, however, that the temperature remains constant at a value only infinitesimally in excess of T_2. During this second isothermal process, P_3P_4 of Fig. 51, radiant energy, in amount H_2, leaves the engine. The decrease in volume, dv, is as in (*a*), assumed to be very small.

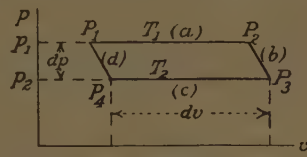

FIG. 51.—Carnot's cycle for black-body radiation in the "ether" engine.

(*d*) Having reached a suitable point P_4, the opening O is closed, and the radiation is further compressed adiabatically until the initial position P_1 is reached corresponding to the initial volume, energy density, and temperature.

The net external work done during this cycle is represented by the area $P_1P_2P_3P_4$ of Fig. 51. If we assume the changes of volume, of pressure, and of temperature to have been very small, this area equals $dp \cdot dv$. (The figure is practically a small parallelogram of length dv and of altitude dp.) Calling the net external work dW, we, therefore, have

$$\begin{aligned} dW &= dp \cdot dv \\ &= \tfrac{1}{3}\, d\psi dv \end{aligned} \qquad (27)$$

by equation (26). Remembering that the heat taken in during the isothermal process P_1P_2 is $\frac{4}{3}\psi dv$, according to equation (25), we may now write the equation, corresponding to equation (22),

$$\frac{dT}{T} = \frac{\frac{1}{3}\, d\psi dv}{\frac{4}{3}\psi dv} \tag{28}$$

$$\therefore \frac{dT}{T} = \frac{1 d\psi}{4\ \psi} \tag{29}$$

a relation between ψ and T which, at once, integrates to

$$4 \log T = \log \psi + \text{constant} \tag{30}$$

or

$$\psi = aT^4 \tag{31}$$

where a is some constant.

Equation (31) states that the energy density of the radiation within an enclosure is proportional to the fourth power of the absolute temperature T. Since the emissive power E of a small opening in the side of the enclosure is proportional to the energy density within the enclosure, *i.e.*, $E \propto \psi$, it follows at once that *the total emissive power of a black body is proportional to the fourth power of its absolute temperature.* We may write, therefore,

$$E = \sigma T^4 \tag{32}$$

where σ is a constant. This equation is of the same form as the empirical equation (20) and is known as the "Stefan-Boltzmann law." The constant σ, known as "Stefan's constant," or as the "Stefan-Boltzmann constant," has a numerical value,[1] determined by experiment (see next section), of 5.709×10^{-5} ergs per square centimeter per second per deg.^{4}, if T is the absolute temperature on the Kelvin scale.

In passing, attention may be called to an important relation which exists between the constant a in equation (31) and the constant σ in equation (32). It may be readily shown that

$$a = \frac{4}{c}\sigma$$

and therefore,

$$\psi = \frac{4}{c} E \tag{33}$$

[1] From the International Critical Tables.

where c is the velocity of light. The proof of this relation is left to the reader.[1] The numerical value of a, computed from the above value of σ, is

$$a = 7.617 \times 10^{-15} \text{ erg cm.}^{-3} \text{ deg.}^{-4}$$

8. Experimental Verification of the Stefan-Boltzmann Law. The importance of the Stefan-Boltzmann law of total radiation has inspired many investigators to check its validity. Among these may be mentioned Lummer and Pringsheim,[2] who studied

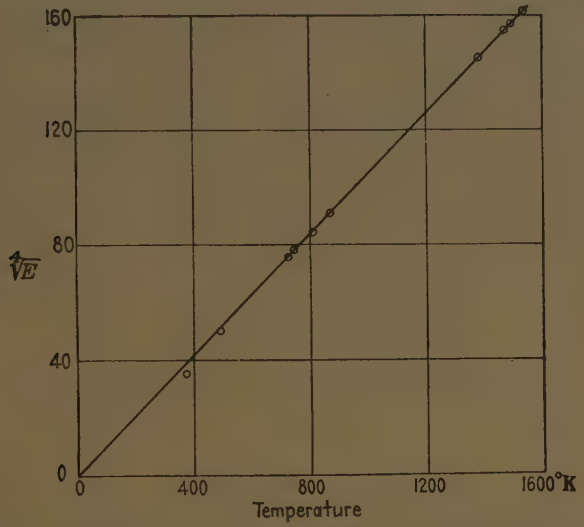

FIG. 52.—Verification of the Stefan-Boltzmann total radiation law.

the total radiation from an experimental black body over a temperature range from 373 to 1535°Abs. Their data are shown

[1] *Hint:* Since the radiation within an enclosure is streaming equally in all directions, it is readily seen that a fraction $d\omega/4\pi$ of the entire radiation within an element of volume dv is streaming in directions which lie inside a small cone of solid angle $d\omega$ described about dv as a center. Accordingly, the flow of radiation through an element dS of the surface of a black body, within a cone of solid angle $d\omega$, the axis of which makes an angle θ with the normal to dS, is given by

$$c\psi dS \cos\theta \frac{d\omega}{4\pi}$$

where c is the velocity of light. From this, the intensity of the radiation i in the direction θ may be computed (see Sec. 2(c), this chapter), and equation (33) follows at once by use of equation (6).

[2] *Ann. Physik*, vol. 63, p. 395 (1897). These experiments are described in PRESTON'S "Theory of Heat."

graphically in Fig. 52, in which the abscissæ are absolute temperatures of the black body as measured with a thermo-element which, in turn, was calibrated (indirectly) against a nitrogen gas thermometer. The ordinates are the fourth roots of the total emissive power E (in relative units) of the black body. Except for the two lowest points (which involved troublesome corrections), the relation between $\sqrt[4]{E}$ and T is seen to be in excellent agreement with the Stefan-Boltzmann law.

From these measurements, Lummer and Pringsheim obtained a value of σ of 5.32 erg cm.$^{-2}$ sec.$^{-1}$ deg.$^{-4}$ Numerous recent investigations[1] have shown that the value of σ is considerably higher than that found by Lummer and Pringsheim, the present accepted value, as quoted above, being $\sigma = 5.709 \times 10^{-5}$ erg cm.$^{-2}$ sec.$^{-1}$ deg.$^{-4}$

From these two constants σ and a, one may compute the total emissive power E of a black body at any temperature, and the energy density ψ of the radiation within an enclosure, by the formulæ

$$E = 5.709 \cdot 10^{-5} T^4 \text{ erg cm.}^{-2} \text{ sec.}^{-1}$$

$$\psi = 7.617 \cdot 10^{-15} T^4 \text{ erg cm.}^{-3}$$

Thus, the total emissive power of a black body at a temperature of 1000°Abs. is

$$E_{1,000} = 5.71 \times 10^{7} \text{ erg cm.}^{-2} \text{ sec.}^{-1}$$

The energy density of the radiation within an enclosure at the same temperature is

$$= 7.62 \times 10^{-3} \text{ ergs per cubic centimeter.}$$

The pressure due to radiation on the walls of such an enclosure is 2.54×10^{-3} dynes per square centimeter.

Note.—A word about temperature measurement: The universally accepted scale of temperature is the Kelvin scale. It cannot be utilized *directly* but is approximated with sufficient accuracy for experiment by a gas thermometer (hydrogen or, for higher temperatures, nitrogen). Due to obvious limitations, it is impossible to use gas thermometers above temperatures of 1300 or 1400°C. It is, therefore, impossible to extend the Kelvin scale, *by means of the gas thermometer*, above this temperature. The several radiation laws—Stefan's and others—are checked experimentally up to 1300 or 1400°C. by use of the gas thermometer. Beyond these temperatures, *the*

[1] For a summary of experimental values of σ and other radiation constants, see W. W. COBLENTZ, *Jour. Opt. Soc. Amer.*, vol. 5, p. 131 (1921) and vol. 8, p. 11 (1924).

laws themselves are used to establish a temperature scale. This procedure is perfectly logical, particularly in the case of Stefan's law, since that law itself is derived by use of the Carnot's cycle, which forms the basis of the Kelvin scale. In other words, excepting as one method may be superior to another experimentally, it should be a matter of indifference, in realizing the Kelvin scale, whether we use a gas thermometer (making corrections for the behavior of the actual gas used so as to make the measurements conform to a *perfect* gas scale, which, in turn, is identical with the Kelvin scale) or whether we use a radiation law, such as Stefan's, which is based upon Carnot's cycle, and which, likewise, should provide a satisfactory means of realizing the Kelvin scale.

9. The Spectral Distribution of Black-body Radiation.—In the discussion in the preceding section on the Stefan-Boltzmann law, it was not necessary to introduce any theories as to the nature of radiation. And the experimental results were found to be in complete agreement with theory. When, however. we

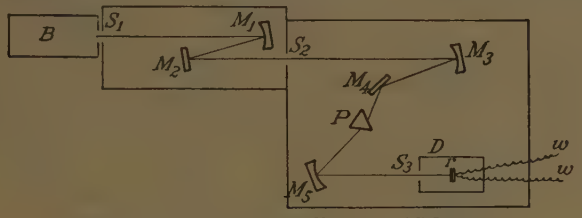

FIG. 53.—The spectroradiometer (*Coblentz*).

come to a discussion of the spectral distribution of the radiation from a black body, we introduce, at once, the concept that radiation consists of a wave motion. Here, classical theories made some progress but could find only a partial solution of the problem.

There have been many investigations to determine experimentally how the distribution of energy in the spectrum of a black body depends both on wave length and temperature. As typical of the apparatus used in making measurements of this kind may be mentioned the spectroradiometer, described by Coblentz[1] and shown diagrammatically in Fig. 53. Radiation from an electrically heated black body B enters the slit S_1, an image of which is thrown on the slit S_2 by means of the concave

[1] GLAZEBROOK: "Dictionary of Applied Physics," vol. IV, p. 554. This contains (pp. 541–572) an excellent account of the determination of the several radiation constants, the verification of the radiation laws and an abstract of radiation theory.

mirror M_1 and the plane mirror M_2.[1] Slit S_2 is placed at the principal focus of the concave mirror M_3, so that the rays reflected from M_3 are parallel. After reflection from the plane mirror M_4, the rays pass through the quartz or fluorite prism P, by which they are dispersed into a spectrum, which is focused at S_3 by the concave mirror M_5. By suitable angular adjustments, radiation of any desired wave length may, thus, be caused to enter S_3 and fall upon the receiving element r of a bolometer, contained in the enclosure D, from which wires ww lead to the measuring apparatus. The temperature of the black body B is measured by a thermo-junction.

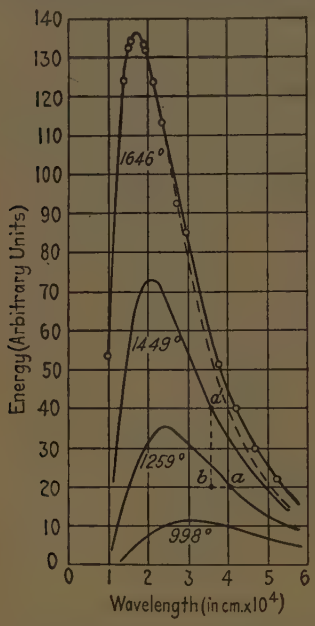

FIG. 54.—Distribution of energy in the spectrum of a black body at various temperatures.

After making necessary corrections for absorption in various parts of the apparatus, curves of the type shown in Fig. 54 are obtained for the energy distribution in the spectrum of a black body at various temperatures. These curves are from the much quoted measurements of Lummer and Pringsheim.[2] The wave lengths λ are in microns (cm.$^{-4}$, symbol μ), the visible region of the spectrum lying at the left of the curves, between 0.4 and 0.8μ. The ordinates are monochromatic emissive powers e_λ (see Sec. 2(b)) in arbitrary units. The temperatures are in degrees (centigrade) absolute. In the curve for the temperature 1646°, the circles represent *actual observations*. (These are omitted in the remaining curves.) It is to be noted: (1) that the energy at each wave length rises rapidly with increase in temperature and (2) that the higher the temperature T the shorter the wave length λ_m at which maximum energy occurs, the relation between λ_m and T being found experimentally to be

$$\lambda_m T = \text{constant} = w$$

[1] All mirrors are silvered on the front face.

[2] *Verhandlungen der Deutschen Physikalischen Gesellschaft*, vol. 1, pp. 23 and 215 (1899) and vol. 2, p. 163 (1900).

This law is known as "Wien's displacement law." We shall discuss it later.

At the time Lummer and Pringsheim reported the measurements quoted in the preceding paragraph, several formula were, or had been, proposed to express e as a function of λ and T. Among these were

1. Wein's formula:[1]

$$e_\lambda = c_1\lambda^{-5}e^{-\frac{c_2}{\lambda T}} \tag{34}$$

2. Thiessen's formula:[2]

$$e_\lambda = c_1\lambda^{-5}(\lambda T)^{\frac{1}{2}}e^{-\frac{c_2}{\lambda T}} \tag{35}$$

3. Rayleigh's formula:[3]

$$e_\lambda = c_1\lambda^{-4}Te^{-\frac{c_2}{\lambda T}} \tag{36}$$

In these formulæ, "e" is the natural base of logarithms, and c_1 and c_2 are constants, not necessarily the same for the several formulæ. The measurements of Lummer and Pringsheim, and the subsequent measurements of Rubens and Kurlbaum[4] at very long wave lengths, proved that none of these formulæ gave values for the energy distribution throughout the entire spectrum which agreed with experiment. For example, although Wien's formula agreed with experiment at short wave lengths, there were systematic deviations on the long-wave-length side of the point of maximum energy, the formula predicting a value too low, as is shown by the dotted line in Fig. 54 for the temperature 1646°. Just how far formulæ such as these, based on classical methods of deduction, were successful, we shall discuss in the next section.

10. The Successes and the Failure of Classical Thermodynamics.—The fact that Wien's law predicts a spectral energy distribution which agrees with experiment over *part* of the wave-length range suggests that it is, *in part* at least, based upon fundamentally correct principles. In this section, we shall consider how far these principles succeeded and where they failed. In this discussion, we shall resort to highly idealized experiments with imaginary apparatus quite impossible of realization. Such

[1] *Ann. Physik*, vol. 58, p. 662 (1896).

[2] *Verhandlungen der Deutschen Physikalischen Gesellschaft*, vol. 2, p. 37 (1900).

[3] *Phil. Mag.*, vol. 49, p. 539 (1900).

[4] *Ann. Physik*, vol. 4, p. 649 (1901).

procedure is, of course, quite permissible in *any* discussion, *provided we test the final conclusions by a real experiment.*

(*a*) *The Wave-length-Temperature Displacement Law.*—Consider a hollow sphere (Fig. 55) radius r_1, with walls which (1) are perfect *specular* reflectors and (2) are capable of expansion so as to increase the radius, say to r_2. Let this sphere be entirely empty initially of all radiation. At the center, we shall imagine a very small spherical radiator b, which is at any specified temperature T and which initially is covered so as to prevent the escape of radiation into the interior of the sphere.

At a given instant, the radiator b is very suddenly uncovered, and radiation begins to stream *radially*, in an expanding spherical wave train, toward the walls of the sphere. We shall allow b to remain in the sphere until the *first* wave of the train, after specular reflection from the walls of the sphere, has returned to b. At this instant, we shall suddenly remove b from the enclosure. We shall then have a train of (spherical) waves (of course, of all wave lengths) extending from the center to the walls and back again.

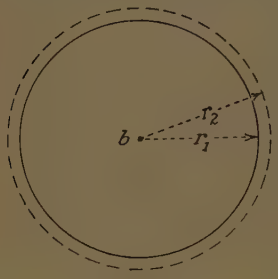

FIG. 55.

These waves, after specular reflection from the walls, will return toward the center, pass to the opposite side, where they will again be reflected, and so will travel back and forth, remaining spherical waves.

If we fix our attention on any one particular wave length λ_1, the number n of those waves between the center and the walls of the sphere is obviously given by

$$n = \frac{r_1}{\lambda_1} \tag{37}$$

Now, imagine the sphere to expand *slowly* until its radius has reached r_2. Because of the change in wave length, by Doppler's principle, when waves are reflected from a receding mirror, we shall have after this expansion *exactly the same number of waves n* in the new radius r_2, the new wave length λ_2 being given by the relation

$$n = \frac{r_2}{\lambda_2} \tag{38}$$

Therefore, combining equations (37) and (38), we have

$$\frac{r_1}{\lambda_1} = \frac{r_2}{\lambda_2} \tag{39}$$

or,

$$\frac{\lambda_1}{\lambda_2} = \frac{r_1}{r_2} \tag{40}$$

which shows that the increase in wave length is proportional to the increase in radius, and this proportionality holds for *any* wave length within the sphere. Since r_2 was *any* new radius, we may generalize equation (39) by writing,

$$\frac{r}{\lambda} = \rho_\lambda \tag{41}$$

where ρ_λ is some constant.

This highly artificial limitation of the radiation within the enclosure to *spherical* waves is, of course, unnecessary, as is also the limitation of the walls to *specular* reflectors. (The walls must, however, be perfect reflectors.) Thus, we might imagine a hollow sphere, with perfect reflecting walls in which is a small opening which can be placed opposite a black body at temperature T. Presently, the sphere will be filled with radiation of density ψ, appropriate to the temperature T. Now close the opening with a perfect reflector, thus imprisoning the radiation, which will travel back and forth in all directions, in general, along chords of the sphere. Because of Doppler's principle, and because the proportionate increase in length of any cord of the sphere, if the sphere be allowed to expand, is the same as the proportionate increase in radius, it is obvious that any expansion will result in an increase in wave length, of any given wave train, in the proportion specified by equation (41). The radiation, both before and after expansion, contains a whole spectrum of wave lengths, but any particular wave length λ_1 before expansion *corresponds to* a particular wave length λ_2 *after* expansion.

Consider, now, such a sphere with perfectly reflecting, extensible walls, filled with (black-body) radiation at temperature T and of density ψ, such that

$$\psi = aT^4$$

If the radius of the sphere be r, and its volume, accordingly, $\frac{4}{3}\pi r^3$, the total energy content U of the sphere is

$$U = \tfrac{4}{3}\pi r^3 \cdot \psi \tag{42}$$

The pressure against the walls of the sphere is $\psi/3$. If the sphere expands adiabatically, this pressure does external work dW, given by[1]

$$\begin{aligned} dW &= \tfrac{1}{3}\psi \cdot 4\pi r^2 dr \\ &= \tfrac{4}{3}\pi\psi r^2 dr \end{aligned} \tag{43}$$

where dr is the increase in radius. This external work will be done at the expense of the internal energy U, which will, therefore, decrease by an amount dU obtained by differentiating equation (42),

$$dU = 4\pi r^2 \psi dr + \tfrac{4}{3}\pi r^3 d\psi \tag{44}$$

since, in equation (42), U is seen to be a function of both r and ψ.

Since the expansion is adiabatic, we may write, with proper regard for signs,

$$dU + dW = 0 \tag{45}$$

Or, substituting for dU and dW from equations (44) and (43), respectively, we have

$$\begin{aligned} 4\pi r^2 \psi dr + \tfrac{4}{3}\pi r^3 d\psi + \tfrac{4}{3}\pi\psi r^2 dr &= 0 \\ \therefore 4\psi dr + r d\psi &= 0 \end{aligned} \tag{46}$$

and therefore

$$\frac{d\psi}{\psi} + 4\frac{dr}{r} = 0 \tag{47}$$

Integrating, we have

$$\log \psi + 4 \log r = \text{constant}$$

or,

$$\psi r^4 = \eta \tag{48}$$

where η is some constant.

Equation (48) shows that as the sphere expands adiabatically the energy density ψ decreases inversely as r^4. This decrease in ψ means a decrease in the temperature of the radiation. For, if the slide over the opening in the sphere be removed after the expansion has taken place, the radiation within the enclosure will be in equilibrium with a black body at a lower temperature. Now, from equation (31), $\psi = aT^4$ and, focusing our attention on *any* wave length λ, we have, from equation (41), a relation between r and that wave length given by $r = \rho_\lambda \lambda$. Putting these values of ψ and r in equation (48) gives

$$aT^4 \rho_\lambda^4 \lambda^4 = \eta \tag{49}$$

$$\therefore \lambda^4 T^4 = \frac{\eta}{a\rho_\lambda^4} = \text{constant}$$

[1] Since there is an increase dv in volume of $4\pi r^2 dr$, and we may apply the general law $dW = pdv$.

or

$$\lambda \cdot T = C_\lambda \tag{50}$$

where C_λ is a constant *for the particular wave length under consideration.*

Equation (50) is a very important equation. It states that if black-body radiation at a particular temperature T_1 be altered by an adiabatic change to some other temperature T_2, then a wave length λ_1 in the radiation at T_1 *corresponds to* a wave length λ_2 in the radiation at temperature T_2, the relation between the two wave lengths being given by $\lambda_1 T_1 = \lambda_2 T_2$, according to equation (50). We may speak of this law as the "wave-length temperature" displacement law.

(*b*) *The Energy-temperature Displacement Law.*—Not only does a given wave length change according to equation (50) when the temperature of the radiation changes adiabatically, but also the *energy* associated with that particular wave length must change because of the necessity of doing external work.

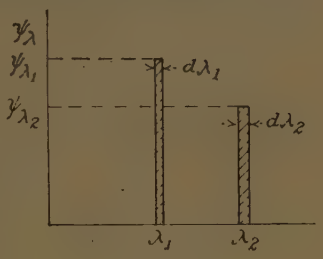

FIG. 56.

If, in the derivation of equation (48), we had filled the sphere not with the total radiation from the black body but with a narrow spectral range of radiation comprised between the wave lengths λ and $\lambda + d\lambda$, the *monochromatic* energy density of this radiation being ψ_λ,[1] we should have been lead by exactly the same kind of reasoning to an equation, analogous to equation (48), of the form

$$(\psi_\lambda d\lambda) r^4 = \eta_\lambda \tag{51}$$

where η_λ is a constant for the particular wave length under consideration. Accordingly, when the expanding sphere has a radius r, let us fix our attention on a narrow spectral range $d\lambda_1$, at λ_1 (Fig. 56). Let the energy density of this radiation be initially $\psi_{\lambda_1} d\lambda_1$ and its temperature T_1. Now, let the sphere expand

[1] ψ_λ is related to ψ in the same way that e_λ is related to E in equation (1); *i.e.*, $\psi = \int_0^\infty \psi_\lambda d\lambda$ and $\psi_\lambda d\lambda$ in equation (51) obviously corresponds to ψ in equation (48).

adiabatically to radius r_2. By this process, λ_1 will be displaced to λ_2 by the relation (equation (40))

$$\frac{\lambda_1}{\lambda_2} = \frac{r_1}{r_2} \tag{52}$$

The wave-length range $d\lambda_1$ will change to $d\lambda_2$, given by

$$d\lambda_2 = d\lambda_1 \frac{r_2}{r_1} \tag{53}$$

The temperature will drop from T_1 to T_2 (equations (50) and (52)), given by

$$\frac{T_1}{T_2} = \frac{\lambda_2}{\lambda_1} = \frac{r_2}{r_1} \tag{54}$$

And, as explained previously, the energy density $\psi_{\lambda_2} d\lambda_2$ will be less than $\psi_{\lambda_1} d\lambda_1$. We wish to find a relation between ψ_λ and T.

From equation (51),

$$\psi_{\lambda_1} d\lambda_1 r_1^4 = \psi_{\lambda_2} d\lambda_2 r_2^4 \tag{55}$$

By equations (53) and (54), we have

$$d\lambda_2 = d\lambda_1 \frac{T_1}{T_2}$$

and by equation (54),

$$r_2 = r_1 \frac{T_1}{T_2}$$

Putting these values of $d\lambda_2$ and r_2 in equation (55), we have

$$\psi_{\lambda_1} d\lambda_1 r_1^4 = \psi_{\lambda_2} d\lambda_1 \frac{T_1}{T_2} r_1^4 \frac{T_1^4}{T_2^4} \tag{56}$$

Therefore,

$$\frac{\psi_{\lambda 1}}{T_1^5} = \frac{\psi_{\lambda 2}}{T_2^5} \tag{57}$$

That is, *the value of the monochromatic energy density ψ_λ is, at corresponding wavelengths, directly proportional to the fifth power of the absolute temperature.* In general, omitting subscripts,

$$\frac{\psi_\lambda}{T^5} = F_\lambda \tag{58}$$

where F_λ is some constant. Since the monochromatic energy density ψ_λ with an enclosure at temperature T is proportional to the monochromatic emissive power e_λ at the same temperature (see equation (33)[1]), we may write, instead of equation (58),

$$\frac{e_\lambda}{T^5} = B_\lambda \tag{59}$$

[1] Equation (33) applies to the relation between *total* emissive power and *total* energy density, but the same relation obviously holds between monochromatic emissive power and monochromatic energy density.

where B_λ is some constant. This relation is the energy-temperature displacement law sought.

(c) *Experimental Confirmation of the Displacement Laws.*— These two displacement laws expressed in equations (50) and (59), namely, $\lambda \cdot T = C_\lambda$ and $e_\lambda T^{-5} = B_\lambda$, give important relations among e_λ, λ, and T, which have been verified by experiment. Thus, to illustrate the applicability of the relations, let the curve in Fig. 57 represent the *experimentally determined* energy distribution in the spectrum of a black body at a temperature T_1. Equations (50) and (59) enable us to compute what the energy distribution ought to be at some other (say higher) temperature

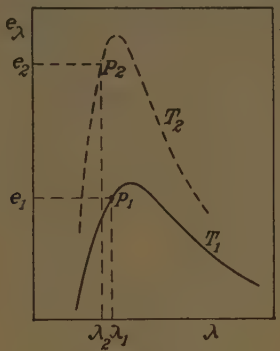

FIG. 57.

T_2, as follows: Choose any wave length λ_1, for which the monochromatic emissive power, at temperature T_1, is e_1, corresponding to point P_1 on the curve. The wave length λ_2, which, at temperature T_2, corresponds to λ_1, is given by equation (50),

$$\lambda_2 = \lambda_1 \frac{T_1}{T_2}$$

And the emissive power e_2, which corresponds to this new wave length at temperature T_2, is given, by equation (59), as

$$e_2 = e_1 \left(\frac{T_2}{T_1}\right)^5$$

These two "displacements" shift point P_1 to P_2, which is a point on the energy-distribution curve for temperature T_2. In this same way, *every* point on the curve at T_1 could be transferred and the energy-distribution curve for T_2 could, thus, be mapped out. It is found that if we start with a known distribution curve, such as that shown for T_1, *the predicted curve for temperature T_2 agrees with the experimentally observed curve for that temperature.*

Thus, turning to Fig. 54, point a on the isotherm for 1259° corresponds to a wave length of 4.1μ and an energy e_λ (*i.e.*, emissive power) of 20. The wave length at temperature 1449° which corresponds to 4.1μ at 1259° is given by

$$\lambda = 4.1 \cdot \frac{1{,}259}{1{,}449} = 3.55\mu$$

This shifts point a to point b. The energy e'_λ at the new wave length and temperature, which corresponds to $e_\lambda = 20$ at 1,259°, is given by

$$e'_\lambda = 20 \cdot \left(\frac{1{,}449}{1{,}259}\right)^5 = 40.5$$

This shifts point b to point a', which falls on the experimentally observed isotherm at 1449°. Points a and a' are, therefore, corresponding points on the two isotherms.

(*d*) *Wien's Displacement Law.*—It follows, from the above, that the *maximum* points of the several isotherms are corresponding points related to each other by the equations

$$\frac{e_m}{T^5} = B \tag{60}$$

and

$$\lambda_m \cdot T = A \tag{61}$$

where A and B are constants; e_m is the maximum (monochromatic) emissive power at temperature T; and λ_m is the wave length at which this maximum emission occurs. Equation (61) is known as "Wien's displacement law," and the constant A is known as "Wein's displacement constant." Its value is obtained by observing the wave length λ_m at which maximum energy occurs in the spectrum of a black body at temperature T. Thus, in Fig. 54, it is seen that maximum energy occurs in the isotherm at 1449° at a wave length of about 2μ (0.0002 cm.), and the product $\lambda_m T$ for this isotherm is about 0.29, where λ_m is expressed in centimeters.

Extensive investigations have shown that Wien's displacement law is confirmed experimentally, the present accepted value[1] of A being

$$A = 0.2885 \text{ cm. deg.}$$

As an illustration of the constancy of A over a wide temperature range may be quoted some measurements by Coblentz:[2]

[1] International Critical Tables.

[2] Bureau of Standards, *Bull.*, vol. 13, p. 459 (1916).

TEMPERATURE, DEGREES K.	$\lambda_m T = A$, CENTIMETER-DEGREES
879	0.2888
953	0.2896
1,077	0.2898
1,175	0.2874
1,277	0.2882
1,353	0.2891
1,452	0.2884
1,540	0.2881
1,663	0.2887

(*c*) Another experimental test for the correctness of the two displacement laws follows from the conjugate relation which

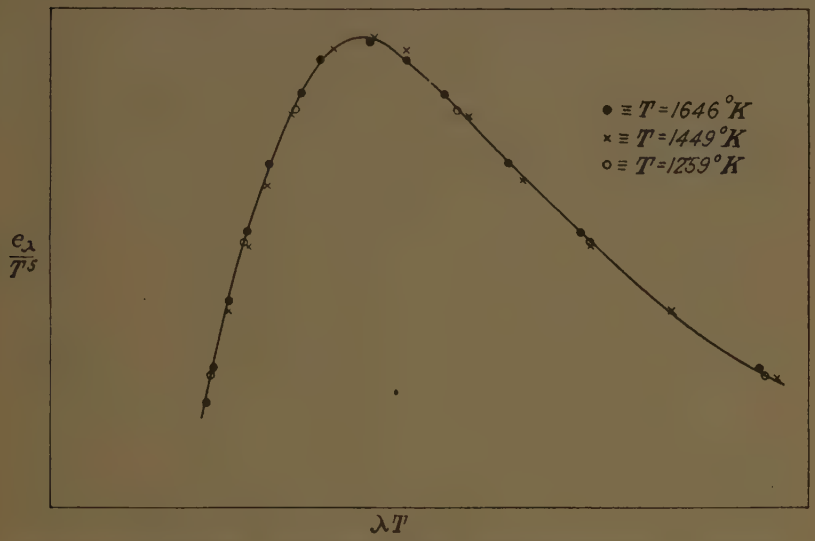

FIG. 58.—Experimental verification of the displacement laws of black-body radiation.

exists between points *a* and *a'*, in Fig. 54. From the steps taken to determine the position of point *a'* from the coordinates of point *a*, it follows that if the ordinates e_λ of any isotherm at temperature T be divided by T^5, and the corresponding abscissæ λ be multiplied by T, then a curve plotted with e_λ/T^5 as ordinates against $\lambda \cdot T$ as abscissæ should be the same for *all* isotherms. There is plotted, in Fig. 58, such a composite curve from data taken from the three isotherms 1259, 1449, and 1646°, of Fig. 54, the solid circles corresponding to 1646°K.; the crosses, to 1449°K.;

and the hollow circles, to 1259°K. It is seen that a (reasonably[1]) smooth curve results.

(*f*) The curve shown in Fig. 58 is extremely significant, for *it represents the limit of success of classical theories in explaining the spectral distribution of energy in the spectrum of a black body.* We have seen, in Sec. (*c*) of this article, that, given an experimentally observed isotherm at one temperature, the isotherm at any other temperature can be successfully predicted. This fact is, in reality, also contained in Fig. 58. *But the classical theories have failed to predict the relation between e_λ and λ in the original isotherm from which others may be computed.* Or, to put the same idea in different form, it is obvious, from Fig. 58, that e_λ/T^5 is *some* function (alike for all wave lengths and temperatures) of $(\lambda \cdot T)$. That is to say,

$$\frac{e_\lambda}{T^5} = f(\lambda \cdot T) \tag{62}$$

where f is the unknown function. In view of the relation between λ and T given by equation (50),

$$\lambda \cdot T = C_\lambda,$$

it is possible to transform equation (62) into the alternative form

$$e_\lambda = C\lambda^{-5} \cdot f(\lambda \cdot T) \tag{63}$$

where C is a constant.

Wien, Rayleigh,[2] and others attempted to evaluate the function $f(\lambda \cdot T)$ and obtained the formulæ previously quoted (equations (34) and (35)). As pointed out previously, these formulæ failed to agree with experiment. The case for classical physics, as based on thermodynamical grounds, therefore, rests with the experimentally correct, but *incomplete*, equation (63). We shall consider, in Secs. 11 to 13, a method of approach to the radiation problem based upon the concepts of statistical mechanics and the law of the equipartition of energy.

11. Degrees of Freedom and the Equipartition of Energy.—(*a*) A gas molecule within an enclosure is *free* to move in a variety of ways: It may, in general, have a motion of translation; a

[1] The original data of Lummer and Pringsheim were given in graphical form only. In obtaining data for Fig. 58 the coordinates e_λ and λ were read directly from the curves of Fig. 54. Since only approximate values were thus obtainable, some scattering of the points in Fig. 58 is to be expected.

[2] For an outline of the arguments of Wien and of Rayleigh see PRESTON'S "Theory of Heat."

motion of rotation; and, *if polyatomic*, the atoms may vibrate with respect to each other. A billiard ball upon the table does not have so great freedom of motion as the gas molecule, for, although the ball has as much freedom of rotation as does the molecule, its motion of translation is confined to a plane. A flat disk sliding upon the ice is not so free as is the billiard ball, for the disk is capable of rotation about only one axis, namely, the vertical axis. A block sliding in a closely fitting groove is still more restricted in its freedom of motion.

Now, it is obvious that the relative freedom of motion of these several bodies can be expressed by giving the number of independent quantities which need be known to express completely the position and orientation of the bodies. Thus, in the case of the block sliding in the groove, its position and orientation is completely specified by one quantity—its distance from some origin. For the disk on the ice, three quantities are required—two to express the position of some point, say the center of gravity, of the disk with respect to some coordinate system on the ice, and one more to specify the orientation of the disk with respect to some fixed line. For the billiard ball, five such independent quantities are required—two for position on the table, and three for orientation. *These separate and independent quantities which need be known to specify completely the position and configuration of the body are called the "degrees of freedom" of the body.* The sliding block has 1 degree of freedom; the disk has 3; and the billiard ball has 5.

This concept of degrees of freedom is readily extended to a *system* of bodies. If we have *three* billiard balls on the table, *fifteen* independent quantities are necessary to express the "position and configuration *of the system.*" Degrees of freedom are additive—the total number of degrees of freedom of a system of bodies is the sum of the number of degrees of freedom posessed by the several bodies which make up the system. If, in a certain volume of gas, we have a mixture of N_1 molecules each with n_1 degrees of freedom, and N_2 molecules each with n_2 degrees of freedom, the total number of degrees of freedom of the system is $n_1N_1 + n_2N_2$.

Now, corresponding to each degree of freedom of a system is a possible motion with which is associated kinetic energy. With sufficient preciseness for our purpose, we may say that *the number of degrees of freedom of a system of bodies is equal to the number*

of independent terms which are necessary to express the kinetic energy of the system as a function of its coordinates. A monatomic gas molecule behaves as if it had a motion of translation only.[1] Accordingly; its kinetic energy is completely expressed with respect to an x-y-z coordinate system by the terms

$$\tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

where v_x, v_y, and v_z refer to the component velocities in the three coordinate directions and m is the mass of the molecule. If there are N monatomic molecules in a given mass of gas, $3N$ such independent terms are necessary to express the kinetic energy of the gas at any given instant. On the contrary, a diatomic gas molecule has 6 degrees of freedom, which we may count up as follows: three for translation (of the center of gravity); two for rotation of the "dumb-bell" shaped molecule about each of a pair of axes at right angles both to each other and to the line joining the atoms;[2] and one for the vibration of the atoms with respect to each other. It would require $6N$ terms to express the kinetic energy of N *diatomic* molecules. For a triatomic molecule, we should have 9 degrees of freedom: 3 degrees of translation; 3 degrees of rotation; and 3 degrees of vibration (on the assumption that each of the three modes of vibration is possible).

(*b*) Let us consider, say, a monatomic gas in an enclosure at a uniform temperature T. According to the kinetic theory of gases, the molecules of the gas are in motion in all possible directions with a wide range of velocities, the average kinetic energies of the molecules being a function of the temperature. The degrees of freedom of such a system may be divided into three groups, corresponding to the three coordinate axes, namely, an x group, a y group, and a z group. The theorem of the *equipartition of energy* now says that *each degree of freedom in one group has, on the average, exactly the same amount of kinetic energy as has, on the average, a degree of freedom in any other group.* For example, let us take a census, or "snapshot," of 1,000 of the gas molecules. Each molecule has a component of velocity in each of the coordinate directions x, y, z. Let v_x, v_y, and v_z be these components, and $\tfrac{1}{2}mv_x^2$, $\tfrac{1}{2}mv_y^2$, $\tfrac{1}{2}mv_z^2$ the corresponding kinetic

[1] As will be seen later, this is probably due to the fact that the moment of inertia of a monatomic gas molecule is negligibly small, so that, even if it does rotate, its rotational kinetic energy may be negligibly small.

[2] Rotation about the axis joining the atoms involves, apparently, no kinetic energy (see preceding note).

energies. The *average* kinetic energy per molecule $\overline{E}_x$ in the x direction for the 1,000 molecules is obtained by adding the terms $\frac{1}{2}mv_x^2$ for all the molecules and dividing by 1,000. And, similarly, for the y and the z components. The theorem of the equipartition of energy states that

$$\overline{E}_x = \overline{E}_y = \overline{E}_z$$

Let us designate by $\overline{E}$ the common value of $\overline{E}_x$, $\overline{E}_y$, and $\overline{E}_z$. Then, if in the gas under consideration there are N molecules each with 3 degrees of freedom, the total kinetic energy of the system, due to the random motion of its molecules, is $3N\overline{E}$. The same principles hold for a diatomic gas, the total kinetic energy, in this case, being $6N\overline{E}$. It is to be noted that in the case of the diatomic gas the average *rotational* energy about each of the two axes is the same as the average *translational* energy in each of the three directions x, y, and z.

If we have an enclosure containing N_1 molecules of a monatomic gas, say argon, and N_2 molecules of a diatomic gas, say hydrogen, each hydrogen molecule should,[1] *on the average*, possess *twice* as much kinetic energy as each argon molecule, since the hydrogen molecule has 6 degrees of freedom while the argon molecule has only 3. If, as before, the average energy per degree of freedom be $\overline{E}$, the total *kinetic* energy of the system, due to the random motion of the molecules, should be $(3N_1 + 6N_2)\overline{E}$.

In this latter case, the average energy $\overline{E}$ associated with the "vibratory" degrees of freedom of the diatomic molecules gives the average *kinetic* energy of vibration. This vibratory motion becomes possible only if we assume that the 2 atoms which make up the molecule are bound together by forces which, normally, hold the 2 atoms in certain fixed equilibrium positions with respect to some fixed point within the molecule. Vibrations take place when this equilibrium is disturbed. Now, the energy of any vibrating system is, in general, part kinetic and part potential, the vibration really consisting of a cyclic interchange of energy from the one form to the other, as, for example, in the simple pendulum. For the simple pendulum it is easily shown that the *time* average of its kinetic energy is exactly equal to the *time* average of its potential energy. Applying this same principle to the vibrations of the diatomic molecule, we see that the average amount of *potential* energy associated with each

[1] That is, if we assume that all of the degrees of freedom are "active." See, however, Chap. VIII, Sec. 10.

"vibratory" degree of freedom is the same as its average *kinetic* energy $\bar{E}$. The total amount of energy associated with the vibratory motion is, therefore, $2\bar{E}$.

If a small crystalline solid be suspended in the enclosure with the gas, the solid soon reaches the temperature of the gas, the molecules of the solid, by virtue of thermal agitation, executing vibratory motions about positions of equilibrium. Each molecule possesses, in respect of these vibrations, 3 degrees of freedom. And if the average kinetic energy per degree of freedom of the molecules of the gas in which the solid is suspended be $\bar{E}$, the law of the equipartition of energy requires that the average *kinetic* energy per degree of freedom *in the solid* shall, also, be $\bar{E}$ and that the average kinetic energy of each molecule of the solid shall be $3\bar{E}$. But the average potential energy is the same as the average kinetic energy. The total (average) energy of each molecule of the solid is, therefore, $6\bar{E}$.

This quantity $\bar{E}$ depends only on temperature and is independent of the nature or state of the substance.

12. Relation between Energy per Degree of Freedom and Temperature.—The average energy per degree of freedom, as discussed in the preceding section, is a very simple function of temperature. This may be shown as follows:

According to the kinetic theory of gases, the pressure P which a gas exerts on an enclosure is given by[1]

$$P = \tfrac{1}{3}\rho\bar{v}^2 \qquad (64)$$

where ρ is the density of the gas and $\bar{v}$ is the "mean square" velocity of its molecules. Since $\rho = nm$, where n is the number of molecules per cubic centimeter in the gas and m is the mass of each molecule, we have

$$P = \tfrac{1}{3}nm\bar{v}^2 \qquad (65)$$

Assume that we are dealing with a monatomic gas at temperature T. Then, the average kinetic energy $\bar{E}_K$ of each molecule of the gas is given by

$$\bar{E}_K = \tfrac{1}{2}\, m\bar{v}^2$$

and we may write, instead of equation (65),

$$P = \tfrac{2}{3}n\bar{E}_K \qquad (66)$$

$\bar{E}_K$ depends on the temperature.

Now,

$$P \cdot V_M = RT \qquad (67)$$

[1] See any textbook on general physics.

where V_M is the volume of a gram-molecule of the gas at temperature T, and R is a universal constant known as the "gas constant," the numerical value of which is 8.315×10^7 ergs per mole per degree, or 1.987 calories per mole per degree. Putting the value of P from equation (66) into equation (67) gives

$$\tfrac{2}{3} n \bar{E}_K V_M = RT \tag{68}$$

The product of n, the number of molecules per cubic centimeter of gas, by V_M, the volume of the gram-molecule, is equal to N_0, the number of molecules in a gram-molecule. That is,

$$nV_m = N_0 \tag{69}$$

N_0, known as *Avogadro's number*, is constant for all substances. Its numerical value is 6.061×10^{23} molecules per gram molecule. Putting this value of N_0 from equation (69) in equation (68) and solving for $\bar{E}_K$, we have

$$\begin{aligned} \bar{E}_K &= \frac{3}{2} \frac{R}{N_0} T \\ &= \tfrac{3}{2} k_0 T \end{aligned} \tag{70}$$

where

$$k_0 \equiv \frac{R}{N_0}$$

k_0 being another universal constant, the numerical value of which is given by

$$k_0 = \frac{8.315 \times 10^7}{6.061 \times 10^{23}} = 1.372 \times 10^{-16} \text{ ergs per molecule per degree}$$

The constant k_0 is known as "Boltzmann's constant," or as the "molecular gas constant."

Equation (70) gives the average kinetic energy of the monatomic molecule which we are considering. As pointed out in the preceding section, such a molecule has 3 degrees of freedom. The average energy per degree of freedom, therefore, *i.e.*, the quantity which we have designated by $\bar{E}$, is obviously

$$\bar{E} = \tfrac{1}{2} k_0 T \tag{71}$$

which is the desired relation between $\bar{E}$ and T.

The theorem of the equipartition of energy thus leads to a very simple way of computing the energy of thermal agitation, kinetic or kinetic plus potential, of a system, provided (1) that the system has a large enough number of degrees of freedom and (2) that temperature equilibrium has been reached. We do not need to specify, at least within certain limits, the various components of the system. We need to know only its temperature

and the number of degrees of freedom involved. Thus, the average energy per degree of freedom in a gas in statistical equilibrium at 300°Abs. is

$$\overline{E}_{300} = \tfrac{1}{2} \times 1.372 \times 10^{-16} \times 300$$
$$= 2.06 \times 10^{-13} \text{ ergs}$$

And the average kinetic energy of translation of a molecule of the gas (3 degrees of freedom) is 6.18×10^{-13} ergs, irrespective of the nature of the molecules. The total kinetic energy of translation is obtained by multiplying this quantity by the number of molecules involved.

(*c*) These deductions from the theorem of the equipartition of energy have been verified in a very striking manner, both qualitatively and quantitatively, by observations on the Brownian movements. One hundred years ago, Robert Brown, an English botanist, noted that minute particles (small enough to be visible only through a high-power microscope) in suspension in liquids undergo continuously random motions, almost as if they were alive. After the development of the kinetic theory of matter, these random motions were explained as due to the continuous, though irregular, bombardment of the particles by the molecules of the liquid. In 1905, Einstein developed a theory of the motion of these particles based upon the concept of the equipartition of energy, according to which their mean kinetic energy of agitation should be exactly the same as the mean kinetic energy of agitation of a molecule of the liquid at the same temperature, which, per degree of freedom, is given by equation (71). Einstein's equation is as follows:[1]

$$\frac{\overline{\Delta S}^2}{\tau} = \frac{2}{K} \cdot \frac{R}{N_0} T \qquad (72)$$

where ΔS is a small distance moved by the particle in a time τ (several seconds) and ΔS^2 is the average square of a large number of such observed values of ΔS; K is a constant depending on the viscosity of the medium in which the particle is suspended and on the size of the particle; R, N_0, and T are, respectively, the gas constant, Avogadro's number, and the temperature. $\overline{\Delta S}^2$ can be observed directly by watching the particle for a long time in the field of the microscope and observing its position at fixed

[1] For a derivation of this equation, and a discussion of its experimental verification, see LOEB: "Kinetic Theory of Gases" (1927) or MILLIKAN: "The Electron."

intervals of time; K can be computed; and it is, thus, possible to determine experimentally R/N_0, which should be numerically equal to the constant k_0 of equation (71). Actually, the value of R/N_0, as determined experimentally by use of equation (72), is combined with the known value of R and a value of N_0 is thus determined from the Brownian movements. The value of N_0 so obtained agrees, almost within the limits of error of measurement, with that obtained by dividing the faraday by the charge on the electron, thus proving that the law of the equipartition of energy, upon which equation (72) is based, is valid and incidentally verifying, beyond doubt, the kinetic theory of matter.

The law of the equipartition of energy is, thus, proved to have a wide validity. And it was suggested by Lord Rayleigh[1] and by Jeans[2] that this law might be applied to the radiation problem by computing the number of modes of free vibrations in the ether in an enclosure and by assuming that with each mode of vibration, or degree of freedom, there is associated, *on the average*, $\frac{1}{2}k_0T$ of kinetic energy and a like amount of potential energy, or a total energy of k_0T per degree of freedom.

13. The Rayleigh-Jeans Radiation Law. (*a*) *Degrees of Freedom Associated with Ether Vibrations.*—Any vibrating system is, in general, capable of a great many modes of vibration. Thus, a violin string or an organ pipe may vibrate not only in its fundamental mode but also in a great many overtones. We may think of these several overtones as the various "degrees of freedom" of the vibrating system.

We may regard an organ pipe as a one-dimensional system, so far as its standing sound waves are concerned, since the vibrations take place longitudinally and in one direction only—namely, parallel to the axis of the pipe. Standing waves may be set up, also, in a "three-dimensional organ pipe," *i.e.*, in a hollow enclosure such as a large concrete-lined room. In this case, too, we may have a great many possible overtones, or modes of vibration. We shall compute the number of such modes of vibration within a given frequency range, per unit volume of the enclosure for sound waves, and shall then apply the results to the analogous case—the standing waves in the ether within an enclosure— and shall, thus, determine the number of degrees of freedom per unit volume of the ether, for a given frequency range. This number

[1] *Phil. Mag.*, vol. 49, p. 539 (1900).
[2] *Phil. Mag.*, vol. 10, p. 91 (1905).

multiplied by the energy per degree of freedom, *assuming the law of equipartition*, should give us the *energy density* of the radiation of that particular frequency.

Since we are not so familiar, in our ordinary experience, with a three-dimensional system of standing waves, it will be instructive to apply the method of computation first to the case of a one-dimensional system, say a stretched string, in which we may have standing waves of a great range of frequencies. Let a string of very great length L (Fig. 59) be stretched between two

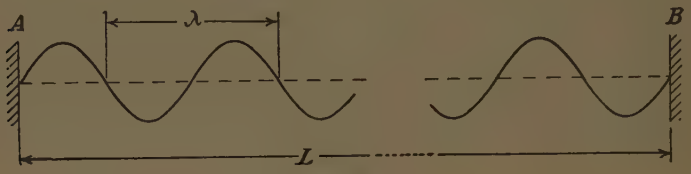

FIG. 59.

supports A and B. The condition that standing waves may be set up requires (1) that A and B (*i.e.*, the ends of the string) shall be nodes of motion and (2) that there shall be an integral number of equal loops between A and B. Since each loop is equivalent to one half of a wave length, we may say that standing waves may occur in the string only for those wave lengths λ defined by

$$\frac{L}{\lambda/2} = i = \frac{2L}{\lambda} \tag{73}$$

where i is some (positive, of course) integer.

For a string of given length and tension, i represents the number of possible modes of vibration of the string for wave lengths λ *or greater*, up to $2L$. As i increases, λ decreases. We now wish to inquire: if i (when i is very large) increases from i to $i + \Delta i$, what is the corresponding change of wave length $\Delta\lambda$ in the system of standing waves? Or, to put the question in somewhat more direct form: how many modes of vibration Δi are possible in the wave-length range λ to $\lambda + \Delta\lambda$? The answer is easily obtained: From equation (73) we have

$$\frac{2L}{\lambda} = i \tag{74}$$

When i changes to $i + \Delta i$, λ changes to $\lambda - \Delta\lambda$, and

$$\frac{2L}{\lambda - \Delta\lambda} = i + \Delta i \tag{75}$$

Subtracting equation (74) from equation (75) and neglecting small quantities (Δi is always taken small compared to i) gives[1]

$$\Delta i = 2L\frac{\Delta\lambda}{\lambda^2} \tag{76}$$

If we divide Δi by L, we have the increase in *i per unit length of string*, for a given change of wave length $\Delta\lambda$, *i.e.*,

$$\frac{\Delta i}{L} = 2\frac{\Delta\lambda}{\lambda^2} \tag{77}$$

Now, associated with each of these modes of vibration i, as here defined, are 2 degrees of freedom, since the vibration is transverse and any segment of the string is free to move in a *plane* at right angles to the string. Representing degrees of freedom by f, we have, therefore,

$$\frac{\Delta f}{L} = 4\frac{\Delta\lambda}{\lambda^2} \tag{78}$$

The number of degrees of freedom per unit length of string in the wave-length range λ *to* $\lambda - \Delta\lambda$ *is* $4\frac{\Delta\lambda}{\lambda^2}$.

The situation is somewhat more complex but involves identically similar principles, when we consider the possible systems of standing waves in a hollow enclosure, say, a cubical box. The essential difference in the two cases is most clearly brought out by discussing first the systems of sound waves in a flat box, a sort of two-dimensional organ pipe. Let $ABCD$ (Fig. 60) represent such a rectangular flat box, and consider a system of plane-parallel sound waves moving parallel to the top and bottom of the box and being reflected, without absorption, from its sides, according to the ordinary law of reflection. A set of waves moving initially in the direction OM_1 (Fig. 61) will, after reflection at the face CD move in the direction M_1M_2. After reflection at M_2, the direction M_2M_3 will be parallel to OM_1, etc. For this group of waves, only four directions of motion are possible (*i.e.*, $\pm OM_1$ and $\pm M_1M_2$).

Let w_1w_1, w_2w_2, w_3w_3 . . . in Fig. 60, represent a series of alternate wave crests and troughs moving initially in the direction

[1] This equation may be derived readily from equation (74) by differentiation: $di = -2L\frac{1}{\lambda^2}d\lambda$. Strictly speaking, this is not permissible, since i is an integer. When, however, i is very large and Δi is very small (*e.g.*, when $i = 700$ and $\Delta i = 2$), the *algebraic* result is the same by differentiation as by the longer process.

AP. After reflection from BC or CD, the direction of motion will be parallel to $+BP'$. If, now, the direction of motion of the waves and the wave length λ be so chosen that the lines w_1w_1 w_2w_2, w_3w_3 . . . , when projected to the sides, divide the side AB into an *integral* number of parts i_1 and the side AD into another integral number of parts i_2 (i_2 may or may not be equal to i_1), we shall have within the box a system of standing waves, similar to those found in an organ pipe.

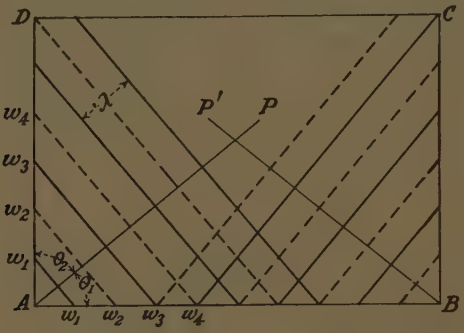

FIG. 60.—Standing sound waves in a "two-dimensional" enclosure.

Let the length of the sides of the box be d_1 and d_2; $\angle PAB = \theta_1$ and $\angle PAD = \theta_2$. Then we shall have standing waves when, *simultaneously*,

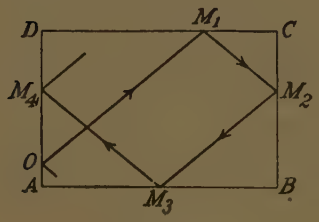

FIG. 61.

$$\frac{d_1 \cos \theta_1}{\lambda/2} = i_1 \text{ and } \frac{d_2 \cos \theta_2}{\lambda/2} = i_2 \quad (79)$$

where i_1, and likewise i_2, may be *any* integer. The conditions for standing waves in the three-dimensional cases, *i.e.*, the hollow *cubical* box each edge of which is of length d is, by obvious extensions of equations (79),

$$\frac{d \cos \theta_1}{\lambda/2} = i_1; \frac{d \cos \theta_2}{\lambda/2} = i_2; \frac{d \cos \theta_3}{\lambda/2} = i_3 \quad (80)$$

where θ_1, θ_2, and θ_3 are the angles which the direction of the wave motion makes with the three edges of the box. The necessary relation among the integers i_1, i_2, and i_3 is readily obtained by making use of the relation that

$$\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 = 1$$

This gives

$$i_1^2 + i_2^2 + i_3^2 = \frac{4d^2}{\lambda^2} \tag{81}$$

That is, *the number of possible modes of vibration within the box corresponding to waves the wave length of which is* λ_m *or greater, is given by the number of possible combinations of integers* i_1, i_2, i_3, *the sum of the squares of which is* $4d^2/\lambda_m^2$ *or less.*

By making use of a simple geometrical construction, we can readily compute to a very close approximation the total number

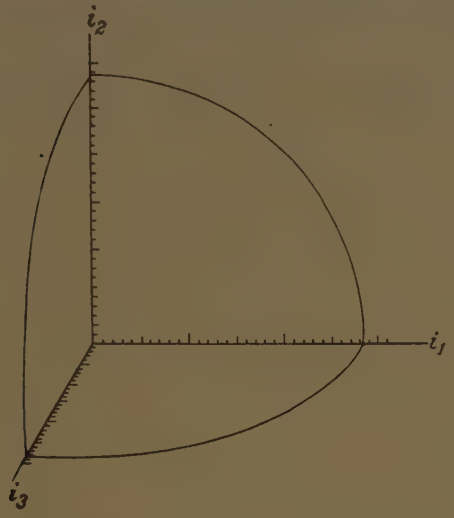

FIG. 62.

of such modes of vibration for wave length λ_m or greater, if we confine ourselves to values of λ_m which are small compared to the dimensions of the box, *i.e.*, to *large* values of the sums of the squares of the integers. Assuming for the wave length the minimum value λ_m, we may write equation (81),

$$i_1^2 + i_2^2 + i_3^2 = \frac{4d^2}{\lambda_m^2} \tag{82}$$

which is the equation of a sphere if we regard i_1, i_2, i_3 as the variables of a rectangular coordinate system, the radius of the sphere being $2d/\lambda_m$. The maximum possible value i_m of each of the three groups of integers will be that corresponding to a zero value for each of the other two, *i.e.*,

$$i_m^2 + 0 + 0 = \frac{4d^2}{\lambda_m^2}$$

Now, lay off, on each axis of a rectangular coordinate system (Fig. 62), equal unit increments of length to represent the integers 1, 2, 3 . . . i_m; 1, 2, 3 . . . i_m; and 1, 2, 3 . . . i_m, respectively. The total possible number n of combinations of the three integers giving sums of squares *equal to or less than* $4d^2/\lambda_m^2$ is, obviously, numerically equal to the volume (in terms of the arbitrary unit of length) of the *octant* of the sphere of radius $2d/\lambda_m$. This number n is, therefore,

$$n = \tfrac{1}{8} \cdot \tfrac{4}{3}\pi\left(\frac{2d}{\lambda_m}\right)^3 \tag{83}$$

Each one of these possible n combinations of integers corresponds to one mode of vibration within the box, *i.e., to* 1 *degree of freedom.* Since d^3 is the volume of the box, the number of degrees of freedom per unit volume of the box is[1]

$$\phi = \frac{n}{d^3} = \frac{4\pi}{3}\frac{1}{\lambda^3} \tag{84}$$

where ϕ is the number of degrees of freedom per unit volume corresponding to vibrations of wave length λ *or greater*, up to $2d$.

Now, just as in the case of the string, we are interested in the number of degrees of freedom (per unit volume) in a wave-length range λ to $\lambda + d\lambda$. This is readily determined by differentiation[2] of equation (84), *viz.*,

$$d\phi = -4\pi\frac{d\lambda}{\lambda^4} \tag{85}$$

which is analogous to equation (76) for the string.

In this discussion, we have been dealing with the longitudinal vibrations of sound waves. An identical analysis will hold for the transverse vibrations of the ether waves, excepting that, in the latter case, because ether waves are transverse, the number of degrees of freedom is twice as great as for longitudinal waves. For the ether, therefore, we may write,[3]

$$d\phi_\lambda = 8\pi\frac{d\lambda}{\lambda^4} \tag{86}$$

where $d\phi_\lambda$ is the number of degrees of freedom per unit volume of the ether in the wave-length range λ to $\lambda + d\lambda$.

[1] We may now drop the subscript in λ_m to make the formula general.

[2] See note, p. 223.

[3] In writing equation (86) we drop the minus sign of equation (85), since, in what follows, we are interested in $d\phi$ only as a positive number.

(*b*) *The Rayleigh-Jeans Formula.*—We are now in position to apply to the radiation problem the law of the equipartition of energy. Consider the radiation within an enclosure the walls of which are at a temperature T, equilibrium having been reached between the radiation and the walls. As previously explained, the radiation then corresponds to black-body radiation at that temperature. Whatever the nature of the radiating and absorbing mechanism of the walls, each degree of freedom of the *entire* system, *walls and ether included*, should have associated with it an average amount of kinetic energy $\frac{1}{2}k_0T$, as given by equation (71). Each "vibratory" degree of freedom has an equal amount of potential energy. The total amount of energy associated with each degree of freedom in the ether should be, therefore, k_0T. By equation (86), the number of degrees of freedom per unit volume in the ether is $8\pi\lambda^{-4}d\lambda$ for the wave-length range λ to $\lambda + d\lambda$. The radiant energy per unit volume in the ether in the wave length λ to $\lambda + d\lambda$, therefore, should be the product of k_0T by $8\pi\lambda^{-4}d\lambda$. This product gives the monochromatic energy density $\psi_\lambda d\lambda$ of the radiation. *That is,*

$$\psi_\lambda d\lambda = 8\pi k_0 T\lambda^{-4}d\lambda \qquad (87)$$

is the equation for the spectral energy distribution in black-body radiation as deduced from the theorem of the equipartition of energy. This is the famous Rayleigh-Jeans formula.

(*c*) *Test of the Rayleigh-Jeans Formula.*—It is obvious, at once, that equation (87) cannot represent the distribution of energy throughout the spectrum of a black body. For a given temperature T, the value of ψ_λ, according to the equation, should vary inversely as the fourth power of the wave length, *increasing rapidly to infinity as the wave length approaches zero;* whereas the actual curves shown in Fig. 54 rise to a maximum with decreasing wave length *and then decrease to zero.* In only one particular does the Rayleigh-Jeans equation agree with the experimental facts: At *long* wave lengths it is found experimentally that the energy *is* inversely proportional to the fourth power of the wave length. For a limited range, the Rayleigh-Jeans expression seems to be in accord with experiment—a circumstance which suggests that, in some particulars, at least, the fundamental principles upon which the deduction of the formula is based must be correct.

But a little consideration will show that the law of the equipartition of energy, as stated above, and the computation of the

number of degrees of freedom in the ether, according to equation (86),

$$d\phi = 8\pi \frac{d\lambda}{\lambda^4}$$

cannot simultaneously be correct. For, if we assume that the ether is perfectly continous, *i.e.*, has no structure such as have material bodies, it should be capable of transmitting[1] waves of wave length varying from infinity to zero. Hence, by integration of equation (86) from $\lambda = \infty$ to $\lambda = 0$, we should find that the number of degrees of freedom in the ether should be infinite. And if the law of the equipartition of energy be correct, we should find that the energy density of black-body radiation, when in equilibrium with the walls of an enclosure at a given temperature, should be vastly greater, really infinitely greater, than the energy density in the walls themselves. Whereas, we find that quite the opposite is the case. Thus, as stated on page 202, the radiation density in the ether in equilibrium with an enclosure at 1000°C., is of the order of 8×10^{-3} ergs per cubic centimeter, while the energy density of the thermal agitation of the molecules of the walls (say of iron) is of the order of 10^{10} ergs per cubic centimeter. Actually, the energy density of the radiation is only an almost imperceptible fraction, 10^{-12}, of the energy density in the walls with which the radiation is in equilibrium; while, according to the Rayleigh-Jeans formula, the reverse ought to be the case.

Apparently, then, classical statistical mechanics has failed to yield a law for the spectral distribution of energy in black-body radiation, just as classical thermodynamics failed. Wien's formula (equation (34))

$$e_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$$

based on the thermodynamic arguments, predicts correct values of e_λ for short wave lengths but gives too low values at long wave lengths. The Rayleigh-Jeans formula (equation (87)), which may be put in the form

$$e_\lambda = C k_0 T \lambda^{-4}$$

where C is a constant, agrees with observed values of e_λ at long wave lengths but gives too high values at short wave lengths.

[1] It is obvious that the minimum wave length of the elastic vibrations which such a body as a crystalline solid can transmit must be at least greater than the average distance between the molecules of the body.

The problem was attacked in various ways by numerous investigators[1] during the first decade of the twentieth century. All deductions based on classical statistical mechanics led to the same incorrect result—the Rayleigh-Jeans formula. Arguments based on classical physics could get no farther than equation (63).

Meanwhile, Planck, in 1900,[2] by introducing a radical innovation quite at variance with previous concepts, discovered a function of λT which gave a formula in complete agreement with experiment. *This was the birth of the quantum theory.* We shall devote the remaining sections of this chapter to a deduction of Planck's formula.

14. Planck's Radiation Law: The Birth of the Quantum Theory. (*a*) *The Statistical Distribution of Energy among Degrees of Freedom.*—In the preceding sections, we have considered only the *average* energy per degree of freedom without paying attention to the actual amount of energy possessed by any particular degree of freedom. Let us consider, again, the case of a gas in an enclosure and at uniform temperature. For a monatomic gas, each molecule has 3 degrees of freedom, one corresponding to each of the three coordinate axes, x, y, and z. We may, as before, divide the *total* number of degrees of freedom into three groups—an x group, a y group, and a z group—the number of degrees of freedom in each group being equal to the total number of molecules in the enclosure.

Of these molecules, some have a very high velocity; some have a very low velocity, theoretically approaching zero; while the great majority have intermediate velocities grouping about a "most probable" velocity, which depends, for a given gas, on its temperature. The law governing the distribution of velocities was deduced by Maxwell and is found in current treatises on the kinetic theory of gases.[3] It would take us too far afield to deduce this law, but the following may help to make its meaning clear: Any very small volume of the gas contains a very large number of molecules. Let us represent the velocity of *each* molecule of this small volume at a particular instant by a vector

[1] For a summary see F. REICHE: "The Quantum Theory," p. 15 (English Translation by Hatfield and Brose, E. P. Dutton and Co.).

[2] M. PLANCK: *Verhandlungen der Deutschen Phys. Gess.*, vol. 2, p. 237, 1900. Also *Ann. Physik*, vol. 4, p. 553 (1901).

[3] JEANS: "The Dynamical Theory of Gases"; LOEB: "The Kinetic Theory of Gases"; LEWIS, W. M. C.: "Kinetic Theory."

drawn from the origin of an x-y-z coordinate system. The totality of such vectors, one for each molecule, will result in a perfectly symmetrical system of vectors, or lines, extending radially from the origin, in all directions, some of the vectors being long, some short, and the majority of them being of intermediate length. Imagine each vector to terminate in a minute sphere, such as s, in Fig. 63 (the z-axis is assumed perpendicular to the plane of the figure). Now divide the whole construction into a series of very thin slices parallel to the yz plane as shown by the dotted lines, the slices being all of the same thickness. And let us count the number of the small spheres (ends of vectors) which we find in each slice. A little reflection will show that the nearer a slice is to the yz plane the more spheres the slice will contain. Representing by n_x the number of spheres found in a particular slice and by p_x the ordinal number of the slice, counting from the one next to the yz plane as $p = 1$

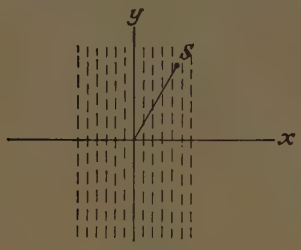

FIG. 63.

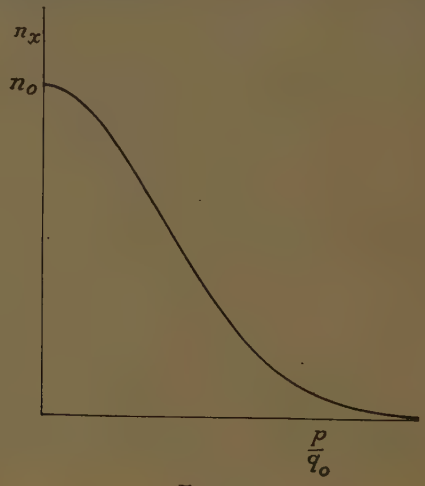

FIG. 64.

(*i.e.*, $p = 11$, say, represents the eleventh slice from the yz plane), a curve plotted between n_x and p_x/q_0 has the form shown in Fig. 64,[1] q_0 being the number of slices in unit length along the

[1] Only one-half of the curve is shown, namely, that in the positive direction of x of Fig. 63. The curve is obviously symmetrical about the y-axis.

x-axis of Fig. 63. Applying the laws of probability, it is deduced in connection with the kinetic theory of gases that this curve has an equation of the form

$$n_x = n_0 e^{-x^2} \tag{88}$$

where $x = p_x/q_0$, e is the Naperian base of logarithms, and n_0 is a constant the significance of which is readily seen by letting $x = 0$. Then, $n_x = n_0$; *i.e.*, n_0 is the value to which n approaches as $x \doteq 0$. To a very close approximation, n_0 may be thought of as the number of spheres in the first slice next to the yz plane, provided q_0 is large.

Since the velocity vectors are distributed perfectly symmetrically about the origin of coordinates in Fig. 63, *both as to direction and magnitude*, it is obvious that curves identical with Fig. 64 would have been obtained if we had taken the slices in Fig. 63 parallel to the xz plane or to the xy plane.

Now, each little sphere counted in Fig. 63 represents 1 degree of freedom—in this case a degree of freedom of the x kind, since the distance of the slices from the yz plane is proportional to the x component of the velocity. And, therefore, n_x is equal to the number of x degrees of freedom associated with each slice. Further p_x, the ordinal number of a given slice, is proportional to the x component of those velocity vectors (all assumed equal) whose end points are found in that particular slice. Likewise, q_0 must be proportional to a unit velocity arbitrarily assumed as a unit in drawing the vectors in Fig. 63. The square of p_x is proportional to the kinetic energy E_x in the x direction[1] of the particular group of molecules whose velocity vectors end in slice p_x. And the square of q_0 is proportional, likewise, to an arbitrary unit of kinetic energy E_0. Remembering that $x^2 = \frac{p_x^2}{q_0^2} = \frac{E_x}{E_0}$ we may, therefore, write, instead of equation (88),

$$n_x = n_0 e^{-E_x/E_0} \tag{89}$$

where n_x is now the number of degrees of freedom possessing energy[2] E_x. Because of the symmetrical distribution of velocities, we have identical expressions for the y group and for the z group of degrees of freedom.

[1] More correctly, "the kinetic energy due to the x-component of the velocity," since energy itself is not a directed quantity.

[2] As noted below, E_x is assumed to be made up of small, *but finite*, increments.

The total number of degrees of freedom is the sum of the three groups. Letting n (without subscript) stand for degrees of freedom, irrespective of direction, and, similarly, replacing E_x by E, we have, with suitable corresponding change in the meaning[1] of n_0,

$$n = n_0 e^{-E/E_0} \tag{90}$$

In the kinetic theory of gases, E_0 is shown to be identical with the quantity which, in preceding paragraphs, we have called the *average* energy per degree of freedom; *i.e.*, $E_0 = \frac{1}{2}k_0T$, where, as in Sec. 12 (equation (71)), k_0 is the Boltzmann constant and T is the temperature. We may, therefore, write

$$n = n_0 e^{-\frac{E}{\frac{1}{2}k_0T}} \tag{91}$$

as the equation which represents the distribution of energy[2] among the various degrees of freedom in a gas in statistical equilibrium at temperature T.

(*b*) *Mean Energy per Degree of Freedom.*—Let us consider a system containing a very large number N of degrees of freedom in the condition of statistical equilibrium to which equation (90)

$$n = n_0 e^{-E/E_0}$$

applies. Let the energy be distributed among the several degrees of freedom in multiples of a small unit of energy ϵ, which, later, we may allow to approach zero, so that $E = p\epsilon$. where p is some integer. We then have

$$n_p = n_0 e^{-p\epsilon/E_0} \tag{92}$$

where n_p is the number of degrees of freedom possessing energy $p\epsilon$, and n_0 is the number of degrees of freedom possessing zero energy. We may then write,

n_0	degrees of freedom possess energy 0
$n_0 e^{-\epsilon/E_0}$	degrees of freedom possess energy ϵ
$n_0 e^{-2\epsilon/E_0}$	degrees of freedom possess energy 2ϵ
$n_0 e^{-3\epsilon/E_0}$	degrees of freedom possess energy 3ϵ

and so forth.

[1] That is, in equation (90), n_0 refers to the total number of degrees of freedom possessing zero energy, *all three groups combined.*

[2] Here, E is to be taken as a multiple of some small quantity of energy ϵ; *i.e.*, $E = p\epsilon$, where p is an integer; n is the number of degrees of freedom possessing p such units of energy. In the limit, of course, ϵ should approach zero.

The total number N of degrees of freedom in the system is the sum

$$n_0 + n_0 e^{-\epsilon/E_0} + n_0 e^{-2\epsilon/E_0} + n_0 e^{-3\epsilon/E_0} + \cdots$$

That is,

$$N = n_0(1 + e^{-\epsilon/E_0} + e^{-2\epsilon/E_0} + e^{-3\epsilon/E_0} \cdots) \quad (93)$$

$$= \frac{n_0}{1 - e^{-\epsilon/E_0}} \quad (94)$$

since the series in the bracket is of the form

$$(1 + x + x^2 + x^3 \cdots) = \frac{1}{1 - x}$$

where $x < 1$. Here $x = e^{-\epsilon/E_0}$, which must always be less than unity.

The total energy W of these N degrees of freedom is obtained by multiplying the number of degrees in each group by the energy per degree possessed by that group and adding the products; thus,

$$W = (n_0 \times 0) + (n_0 e^{-\epsilon/E_0} \times \epsilon) + (n_0 e^{-2\epsilon/E_0} \times 2\epsilon) + (n_0 e^{-3\epsilon/E_0} \times 3\epsilon) + \cdots$$

$$= n_0 \epsilon e^{-\epsilon/E_0}(1 + 2e^{-\epsilon/E_0} + 3e^{-2\epsilon/E_0} + \cdots) \quad (95)$$

$$= \frac{n_0 \epsilon e^{-\epsilon/E_0}}{(1 - e^{-\epsilon/E_0})^2} \quad (96)$$

since the bracket, in equation (95), is of the form

$$(1 + 2x + 3x^2 + 4x^3 \cdots) = \frac{1}{(1 - x)^2}$$

when $x < 1$

The average energy $\overline{U}$ per degree of freedom of these N degrees of freedom is

$$\overline{U} = \frac{W}{N} \quad (97)$$

Putting in equation (97) the value of W from equation (96) and the value of N from equation (94), we have

$$\overline{U} = \frac{\epsilon e^{-\epsilon/E_0}}{1 - e^{-\epsilon/E_0}} \quad (98)$$

$$\therefore \overline{U} = \frac{\epsilon}{e^{\epsilon/E_0} - 1} \quad (99)$$

by dividing both numerator and denominator of equation (98) by $e^{-\epsilon/E_0}$.

If the energy unit ϵ be assumed to have a small, *but still finite*, value, equation (99) gives the average energy per degree of freedom. But if, as we would ordinarily assume in the kinetic theory of gases, the value of $\bar{U}$ is obtained only when ϵ approaches zero, *i.e.*, if we assume that there is *no finite lower limit* to the possible *difference* in energy between molecules, we find, from equation (99), when[1] $\epsilon = 0$,

$$\bar{U} = E_0$$

in agreement with the previous statement with regard to the meaning of E_0, namely, that E_0 is the mean energy per degree of freedom.

(*c*) *Planck's Formula.*—We shall assume that the equation (99)

$$\bar{U} = \frac{\epsilon}{e^{\epsilon/E_0} - 1}$$

is of general validity in giving the average energy per degree of freedom *in any system.* Let us consider once more a hollow enclosure which contains radiation in equilibrium with the walls of the enclosure, all at a temperature T. The radiation comprises a continuous spectrum of frequencies covering a wide range. The walls are absorbing and reemitting this radiation by means of an atomic mechanism the nature of which we need not specify in detail but which, if radiation be electromagnetic, probably consists of vibrating electric systems of some kind. The frequencies of these "atomic oscillators," as we may call them, each of which has a particular natural frequency, must, all together extend continuously over a range of frequencies at least as wide as does the radiation with which the oscillators are in equilibrium. And it is reasonable to assume that the *radiation* within a frequency range ν to $\nu + d\nu$ must be in equilibrium, irre-

[1] If ϵ is put equal to zero in the right-hand side of equation (99), the value of $\bar{U}$ is 0/0. If

$$\frac{f(x)}{F(x)} = \frac{0}{0}$$

when $x = 0$, the value of the indeterminate may be found by putting $x = 0$ in

$$\frac{f'(x)}{F'(x)}$$

where $f'(x)$ and $F'(x)$ are the derivatives with respect to x of the functions $f(x)$ and $F(x)$.

spective of the presence in the system of other frequencies, with the group of *oscillators* whose frequencies cover the same range ν to $\nu + d\nu$.

We may think of these oscillators as possessing 1 degree of freedom each, or we may think of them as possessing several degrees of freedom each. In any event, let us assume that equation (99)

$$\overline{U} = \frac{\epsilon}{e^{\epsilon/E_0} - 1}$$

gives the average energy $\overline{U}$ per degree of freedom of the oscillators, where E_0, taking into account *both kinetic and potential* energy, has the value

$$E_0 = k_0 T$$

That is, let

$$\overline{U}_\nu = \frac{\epsilon}{e^{\epsilon/k_0 T} - 1} \tag{100}$$

where now $\overline{U}_\nu$ is the average energy per degree of freedom of the group of oscillators found in the frequency range ν to $\nu + d\nu$.

Because of the assumed equilibrium between the radiation and the oscillators, $\overline{U}_\nu$ must also be the average energy per degree of freedom in the group of radiation frequencies lying between ν and $\nu + d\nu$. Corresponding to this frequency range $d\nu$ is a wave-length range $d\lambda$, and, for convenience, we shall change the subscript of $\overline{U}$ and let $\overline{U}_\lambda$ equal the average energy per degree of freedom in the ether vibrations in the wave-length range λ to $\lambda + d\lambda$.

In Sec. 13 (*a*), we have computed the number of degrees of freedom per unit volume $d\phi_\lambda$ in the wave-length range λ to $\lambda + d\lambda$, *viz.* (equation (86)),

$$d\phi_\lambda = 8\pi \frac{d\lambda}{\lambda^4}$$

If each degree of freedom has energy $\overline{U}_\lambda$, the total radiant energy per unit volume in the range λ to $\lambda + d\lambda$ is given by

$$\psi_\lambda d\lambda = \overline{U}_\lambda \cdot d\phi_\lambda \tag{101}$$

Or, putting into equation (101) the values of $\overline{U}_\lambda$ and $d\phi_\lambda$, we have

$$\psi_\lambda d\lambda = \frac{8\pi}{\lambda^4} \cdot \frac{\epsilon}{e^{\epsilon/k_0 T} - 1} d\lambda \tag{102}$$

an equation which should represent the relation among ψ_λ, λ, and T in black-body radiation.

It now remains to interpret ϵ, the small, arbitrary element of energy which we used in deriving equation (99). According to classical mechanics and the law of the equipartition of energy, ϵ should be an infinitesimal quantity, *i.e.*; as stated on page 232, there should be no finite lower limit to the possible difference in energy between the several degrees of freedom. The value of $\psi_\lambda d\lambda$, in equation (102), should, therefore, be obtained by letting ϵ approach zero. It is readily seen that when ϵ is zero, equation (102) reduces to

$$\psi_\lambda d\lambda = 8\pi k_0 T \lambda^{-4}\, d\lambda \qquad (103)$$

a result identical with equation (83), *the Rayleigh-Jeans formula, which, as we know, is in complete disagreement with experiment except for very long waves.* Something wrong somewhere!

When theory and *unimpeachable* experimental evidence disagree, *theory must be modified.* Accordingly, let us compare the incomplete formula, equation (63),[1] which, so far as it goes, *does* agree with experiment, with equation (102), *viz.*,

$$\psi_\lambda d\lambda = C_1 \lambda^{-5} f(\lambda \cdot T) d\lambda \qquad (63')$$

$$\psi_\lambda d\lambda = 8\pi \lambda^{-4} \frac{\epsilon}{e^{\epsilon/k_0 T} - 1} d\lambda \qquad (102)$$

The two formulæ differ in two respects: (1) Equation (63′) has λ^{-5}, while equation (102) has λ^{-4}; (2) the fraction

$$\frac{\epsilon}{e^{\epsilon/k_0 T} - 1}$$

in equation (102), *as it now stands*, is a function of T and not of $\lambda \cdot T$, as required by equation (63′). ***Both of these differences would at once disappear, if, in equation (102), instead of allowing ϵ to approach zero, we were to disregard classical principles and were to put ϵ proportional to*** $1/\lambda$. ***This requires that ϵ shall be a finite quantity.*** We therefore put

$$\epsilon \propto \frac{1}{\lambda}$$

or,

$$\epsilon = \alpha \frac{1}{\lambda} \qquad (104)$$

[1] In rewriting equation (63) here, to compare it with equation (102), we have written ψ_λ in place of e_λ, with a suitable implied change in the constant c_1. This is permissible, since $\psi_\lambda \propto e_\lambda$, as pointed out by equations (33).

where α is a proportionality constant. In terms of frequency ν, instead of wave length λ, this is equivalent to assuming, since $\lambda = c/\nu$ ($c \equiv$ velocity of light),

$$\epsilon = \frac{\alpha}{c}\nu = h\nu \tag{105}$$

where $h = \alpha/c$ is another constant.

Putting the value of ϵ, from equation (104), into equation (102), we have

$$\psi_\lambda d\lambda = 8\pi\lambda^{-5}\frac{\alpha}{e^{\alpha/k_0\lambda T} - 1}d\lambda \tag{106}$$

which is of exactly the form required by equation (63), since, in equation (106), we have λ^{-5}, and the fraction *is* now a function of $\lambda \cdot T$. The equation is more usually written in the form, since $\alpha = ch$,

$$\psi_\lambda d\lambda = 8\pi ch\lambda^{-5}\frac{1}{e^{ch/\lambda k_0 T} - 1}d\lambda \tag{107}$$

This is one form of the famous Planck equation for the spectral energy distribution in black-body radiation. An alternative form of this equation is obtained by replacing wave length λ by frequency ν as follows:

$$\lambda = \frac{c}{\nu} \qquad \text{and} \qquad d\lambda = -\frac{c}{\nu^2}d\nu$$

This gives

$$\psi_\nu d\nu = 8\pi h\frac{\nu^3}{c^3}\frac{1}{e^{h\nu/k_0 T} - 1}d\nu \tag{108}$$

Before proceeding to discuss these equivalent formulæ (equations (107)) and (108), it is pertinent to emphasize the radical nature of the assumption $\epsilon = h\nu$ (equation (105)), *which marks the birth of the quantum theory.* According to the older concepts, including the electromagnetic theory of radiation, the interchange of energy between two "systems," as, for example, between one gas molecule and another or between radiation and matter, should be a perfectly *continuous* process. Thus, if one could follow the "history" of a particular gas molecule and observe its kinetic energy at short intervals of time over a very long period, one would find, of course, that its energy varied over enormously wide limits. But if the numerical values of the energy observed at the various instants were to be arranged in a sequence as to order of magnitude, this sequence, on the concept of the equiparti-

tion of energy, would become more and more *continuous* as the number of observations becomes greater. Or, if, instead of observing a single molecule over a long period, one were to observe, at a given instant, the kinetic energy of a very large number of gas molecules or of the above-mentioned oscillators, chosen at random, one ought to find that a similar sequence of values of energy would approach more and more nearly to continuity as the number of observations becomes larger. This continuity of these energy values is not only in accord with, but is also imperatively demanded by, classical physics. For example, the electric and magnetic vectors in a light wave may have any values whatsoever, *from zero up;* and, accordingly, the wave may have any intensity, *from zero up.* Further, the emission and absorption of this energy by the walls of an enclosure should, likewise, be a perfectly continuous process.

But the assumption contained in equation (105)

$$\epsilon = h\nu$$

is *completely* at variance with this older doctrine of continuity. According to this assumption, the numerical sequence of the values of the energy of a large number of the oscillators, of, say, a particular frequency ν, is a *discontinuous series increasing by equal jumps* ϵ, *from zero up.* Some oscillators would be found to have zero energy; others would have energy ϵ; still others, energy 2ϵ, 3ϵ, etc. Not a single oscillator would be found which had energy 1.75ϵ or 3.94ϵ. These oscillators are in equilibrium with radiation of the same frequency in the enclosure, the several degrees of freedom of which, therefore, must, likewise, possess energy 0, 1ϵ, 2ϵ, 3ϵ, or 4ϵ, etc. The interchange of energy between the oscillators and the radiation must take place in multiples of ϵ, *i.e.*, of $h\nu$, *whatever the nature of radiation, of the oscillators, or of the mechanism of the interchange.*

The difference between the two views is rather crudely illustrated by the difference between putting very fine sand and marbles all of equal mass into a bag. The mass of sand in the bag may be adjusted to any desired value whatever, at least so far as ordinary weighing apparatus goes; while the mass of marbles in the bag must always be an integer multiple of the mass of one marble. The analogy is worth carrying further: Even in the case of the sand, if we were limited either in filling or in emptying the bag to the use of a cup of certain size and to transferring the

sand, in or out, only by cupfuls, we should find that the mass of sand in the bag was an integer multiple of the mass of a cupful. The *process* of filling, rather than the material involved, *may be responsible for this integer relation.* But we must remember that, even in the case of the marbles, an ingenious small boy with a hammer might get 3.94 marbles into the bag!

That Planck's postulate is in direct opposition to the law of the equipartition of energy is clearly brought out by considering the equation (100) for the average energy $\overline{U}_\nu$ of a single oscillator, or of a degree of freedom of ether vibration of frequency ν,

$$\overline{U}_\nu = \frac{\epsilon}{e^{\epsilon/k_0T} - 1}$$

which, by replacing ϵ by $h\nu$, becomes

$$\overline{U}_\nu = \frac{h\nu}{e^{h\nu/k_0T} - 1} \qquad (100a)$$

In the oscillator-ether system are degrees of freedom of various kinds: oscillators and ether vibrations of many different frequencies. According to the classical theories, *i.e.*, equipartition of energy and continuity, each degree of freedom of one kind should have exactly the same energy, *on the average*, as a degree of freedom of any other kind. That is, the vibrations of high frequency within a given frequency range should have the same average energy as vibrations of a lower, or any other, frequency. This at once follows from equation (100*a*), by introducing the principle of continuity, which, as above stated, requires that

$$\epsilon = h\nu = 0$$

Putting $h\nu = 0$ in equation (100*a*) gives, as we have seen,

$$\overline{U}_{\nu_{\epsilon \doteq 0}} = k_0T$$

which shows that, on the classical theory, the energy per degree of freedom is independent of frequency and is the same for all frequencies.

But if $h\nu$ cannot be zero but is, as Planck assumed, a finite quantity, *then* $\overline{U}_\nu$ *varies with frequency, and there is no longer equipartition of energy among the degrees of freedom of* ***different*** *frequencies.* For very high frequencies, *i.e.*, for short wave lengths, U_ν becomes very small: in the limit, when $\nu = \infty$, $\overline{U}_\nu = 0$, as may be shown by putting $\nu = \infty$ in equation (100*a*). Accordingly, in spite of the fact that the number of degrees of

freedom $d\phi_\lambda$ for a given wave-length range $d\lambda$ increases very rapidly as λ becomes smaller, (equation (86)), the total energy included in that wave-length range decreases, as is required by experiment. On the other hand, for small values of ν, *i.e.*, for large values of λ, $\bar{U}_\nu$ approaches k_0T. The energy per degree of freedom, therefore, ranges all the way from zero for $\lambda = 0$ to k_0T at very long wave lengths. This assumes, of course, the validity of the computation for the number of degrees of freedom per unit volume

$$d\phi_\lambda = 8\pi \frac{d\lambda}{\lambda^4}$$

an assumption which seems justified in view of the fact that it is one of the important factors leading to Planck's equation.

In passing, it may be remarked that the principle of equipartition is retained in a restricted sense. It *is* assumed that the average energy $\bar{U}_\nu$ of an oscillator of frequency ν is the same as the average energy of ether vibrations of the *same* frequency. In other words, there is equipartition of energy, of a kind, among degrees of freedom *of the same frequency*, although, even here, the *distribution* of energy among the oscillators is discontinuous.

It is worth commenting on the fact that Planck's revolutionary assumption $\epsilon = h\nu$ was not based upon logical reasoning following the ordinary lines of classical physics. Quite the contrary: *the assumption was an attempt, entirely empirical, to bring the deductions of classical physics into harmony with experiment.* And the attempt was most astonishingly successful.

(*d*) *Verification of Planck's Law and Evaluation of the Constants h and* k_0.—Equation (107)

$$\psi_\lambda d\lambda = 8\pi ch\lambda^{-5}(e^{ch/k_0\lambda T} - 1)^{-1}d\lambda$$

contains three constants c, the velocity of light; k_0, Boltzmann's constant, the numerical value of which is (p. 219) 1.372×10^{-16} (in c.g.s. units); and a third constant h, which has come to be known as "Planck's constant." If this equation for the relation among ψ_λ, λ, and T be the correct one, it should be in agreement with the following experimentally correct relations:

1. Wien's law at short wave lengths.
2. The Rayleigh-Jeans law at long wave lengths.
3. Wien's displacement law: $\lambda_m \cdot T = \text{constant}$.
4. The Stefan-Boltzmann law of total radiation: $\psi = aT^4$

That Planck's equation coincides with Wien's law at short wave lengths is readily seen. For a given value of the temperature T, the exponent of e, namely $\frac{ch}{k_0\lambda T}$, can be made to assume any positive value by choosing a sufficiently small value of λ, since c, h, and k_0 are constants. The term

$$e^{ch/k_0\lambda T}$$

may, therefore, be made very large compared to unity. For such small values of λ, we may write,

$$\psi_\lambda d\lambda = 8\pi ch\lambda^{-5}e^{-ch/k_0\lambda T}d\lambda \qquad (109)$$

which is identical with Wien's equation

$$\psi_\lambda d\lambda = c_1\lambda^{-5}e^{-c_2/\lambda T}d\lambda$$

provided[1] we put $c_1 = 8\pi ch$
and

$$c_2 = \frac{ch}{k_0}$$

Considering both λ and T to vary, *Planck's equation is practically identical with Wien's for values of* $\lambda \cdot T$, *which are small compared to* ch/k_0.

At sufficiently large values of λ, or, more generally, of $\lambda \cdot T$, the exponent of e, namely,

$$\frac{ch}{k_0\lambda T}$$

becomes small. Expanding[2] $e^{ch/k_0\lambda T}$ and dropping terms involving the square and higher powers of the small quantity $\frac{ch}{k_0\lambda T}$, we have

$$\frac{1}{e^{ch/k_0\lambda T} - 1} = \frac{k_0\lambda T}{ch}$$

Putting this value in Planck's equation gives, for long wave lengths,

$$\psi_\lambda d\lambda = 8\pi k_0 T\lambda^{-4}d\lambda$$

which is identical with the Rayleigh-Jeans formula, the latter, as has been pointed out, giving correct values of ψ_λ for long wave lengths.

[1] Note that, in writing Wien's equation here, we are again using ψ_λ and e_λ interchangeably, with the usual implied change in the constant c_1.

[2] $e^x = 1 + x + \frac{x^2}{\underline{2}} + \frac{x^3}{\underline{3}} + \cdots$

That Planck's formula yields Wien's displacement law

$$\lambda_m \cdot T = \text{constant}$$

where λ_m is the wave length at which the energy density ψ_λ is a *maximum*, follows, at once, from differentiating ψ_λ with respect to λ and putting the derivative equal to zero. Writing Planck's equation,

$$\psi_\lambda = c_1\lambda^{-5}(e^{ch/k_0\lambda T} - 1)^{-1}$$

(where $c_1 \equiv 8\pi ch$), we have

$$\frac{d\psi_\lambda}{d\lambda} = -5c_1\lambda^{-6}(e^{ch/k_0\lambda T} - 1)^{-1} + c_1\lambda^{-5}(e^{ch/k_0\lambda T} - 1)^{-2}e^{ch/k_0\lambda T}\frac{ch}{k_0 T}\lambda^{-2}$$

Putting this derivative equal to zero, and designating by λ_m the value of the wave length for which ψ_λ is a maximum, we have, after simplifying,

$$\left(1 - \frac{ch}{5k_0\lambda_m T}\right)e^{ch/k_0\lambda_m T} = 1 \tag{110}$$

Equation (110) is of the form

$$\left(1 - \frac{x}{5}\right)e^x = 1 \tag{111}$$

where

$$x \equiv \frac{ch}{k_0\lambda_m T}$$

Equation (111) has two roots[1]: $x = 0$; and $x = 4.965$. In the former root ($x = 0$) we are not interested. From the latter, we have

$$\frac{ch}{k_0\lambda_m T} = 4.965$$

or,

$$\lambda_m \cdot T = \frac{ch}{k_0 \times 4.965} \tag{112}$$

which, since the right-hand side is constant, is *in complete agreement with Wien's displacement law.*

[1] The value of x in equation (111) may be determined by Newton's method. SILBERSTEIN: "Synopsis of Applicable Mathematics," p. 85.

The experimental value of $\lambda_m \cdot T$ is 0.2885 cm.-degree, (see p. 212). Putting this value into equation (112) and treating both constants h and k_0 as unknowns, we may solve for a numerical value of h/k_0, *viz.*, ($c = 2.998 \times 10^{10}$),

$$\frac{h}{k_0} = \frac{4.965 \times 0.2885}{2.998 \times 10^{10}} = 4.778 \times 10^{-11} \text{ degree-second} \quad (113)$$

To compare Planck's formula with the Stefan-Boltzmann law of total radiation, it is necessary to integrate $\psi_\lambda d\lambda$ over the range of wave lengths from $\lambda = 0$ to $\lambda = \infty$; *i.e.*,

$$\psi = aT^4 = \int_0^\infty \psi_\lambda d\lambda \quad (114)$$

The integration is somewhat more readily performed by using equation (108), it being obvious that

$$\int_\infty^0 \psi_\nu d\nu = \int_0^\infty \psi_\lambda d\lambda$$

We write, therefore,

$$\psi = \int_\infty^0 \psi_\nu d\nu = \frac{8\pi h}{c^3} \int_\infty^0 \nu^3 (e^{h\nu/k_0T} - 1)^{-1} \, d\nu \quad (115)$$

To integrate this expression, first expand the bracket under the integral, as follows:

$$\frac{1}{e^{h\nu/k_0T} - 1} = e^{-\frac{h\nu}{k_0T}} + e^{-2\frac{h\nu}{k_0T}} + e^{-3\frac{h\nu}{k_0T}} \cdots$$

Equation (115) then becomes

$$\psi = \frac{8\pi h}{c^3} \int_\infty^0 \nu^3 (e^{-\frac{h\nu}{k_0T}} + e^{-2\frac{h\nu}{k_0T}} + e^{-3\frac{h\nu}{k_0T}} + \cdots) d\nu \quad (116)$$

This can be integrated term by term. Take, for example, the first term (omitting the constant $8\pi h/c^3$),

$$\int_\infty^0 \nu^3 e^{-h\nu/k_0T} \, d\nu.$$

Letting $-h\nu/k_0T \equiv z$, a new variable, we can write this integral in the form,

$$\left(\frac{k_0T}{h}\right)^4 \int_\infty^0 z^3 e^z dz$$

Using the standard form,[1]

$$\int x^m e^x dx = x^m e^x - m \int x^{m-1} e^x dx$$

[1] See any table of integrals.

one finds, by straightforward calculation, after putting in the limits,[1] that

$$\left(\frac{k_0T}{h}\right)^4\int_\infty^0 z^3e^z dz = 6\left(\frac{k_0T}{h}\right)^4$$

Similarly, for the *second* term of equation (116), one finds

$$6\left(\frac{k_0T}{h}\right)^4\frac{1}{2^4}$$

and for the *third*,

$$6\left(\frac{k_0T}{h}\right)^4\frac{1}{3^4}$$

and so on.

The complete integral of equation (116) thus becomes

$$\psi = \frac{8\pi h}{c^3}\cdot 6\left(\frac{k_0T}{h}\right)^4\left(1+\frac{1}{2^4}+\frac{1}{3^4}+\frac{1}{4^4}+\cdots\right)$$

$$= \left[\frac{48\pi}{c^3}\cdot\frac{k_0^4}{h^3}\cdot 1.082\right]T^4 \qquad (117)$$

Since the square bracket of equation (117) contains only constant terms, we see that equation (117) *is identical in form with the Stefan-Boltzman law for total radiation,*

$$\psi = aT^4$$

and, that, therefore,

$$a = \frac{48\pi}{c^3}\cdot\frac{k_0^4}{h^3}\cdot 1.082$$

The experimentally determined value of a (see p. 201) is 7.617×10^{-15} ergs-cm.$^{-3}$-deg.$^{-4}$. Therefore, in c.g.s. units,

$$\frac{h^3}{k_0^4} = 7.948\times10^{-16} \qquad (118)$$

These two numerical relations between h and k, *viz.*,

$$\frac{h}{k_0} = 4.778\times10^{-11} \qquad (113)$$

$$\frac{h^3}{k_0^4} = 7.948\times10^{-16} \qquad (118)$$

[1] In evaluating the several terms resulting from this integration, it will be necessary to obtain the value of the indeterminate ∞/∞ by successive differentiation of numerator and denominator.

when solved simultaneously for h and k_0, give

$$k_0 = 1.344 \times 10^{-16} \text{ ergs per degree},$$
$$h = 6.423 \times 10^{-27} \text{ erg-seconds} \qquad (119)$$

The value of k_0 as determined by dividing the gas constant R by the number of atoms in a gram-atom N_0 is (see p. 219) 1.372×10^{-16}, *a value which differs by only 2 per cent*[1] *from the value computed from radiation data on the basis of Planck's formula.* This numerical agreement alone, although not quite within the limits of experimental error, is so significant as to give very great weight to Planck's formula and its general underlying principles. To this confirming evidence must be added the fact that Planck's formula yields Wien's law for short wave lengths, the Rayleigh-Jeans law for long wave lengths, the Wien's displacement law, and the Stefan-Boltzman total radiation law. And this confirmation includes the confirmation of the revolutionary postulate which, alone, distinguishes Planck's result from its predecessors, namely,

$$\epsilon = h\nu$$

But what is the nature of the constant h which is contained in Planck's assumption and the numerical value of which is found above, to be 6.423×10^{-27}? That is a question which modern physics is trying to answer. We know a great deal more about the *numerical value* of h than of its *physical significance.* With regard to the latter, although various statements about h take on a great variety of forms, they boil down to about this: $\epsilon = h\nu$! Or, in words, "h is the constant, dimensions erg-second, which multiplied by frequency ν gives a quantum of energy of that frequency." Not a very "satisfying *physical* definition."

[1] It is interesting to see whether Wien's formula in the form given in equation (109) (*i.e.*, Planck's formula for short waves) would give values of h and k_0 in agreement with experiment. Deriving from equation (109) (instead of equation (108)) the expression for $\lambda_m T$ corresponding to equation (112), one finds

$$\lambda_m T = \frac{ch}{5k_0}$$

Similarly, instead of equation (117), one finds

$$\psi = \frac{48\pi}{c^3} \frac{k_0^4}{h^3} T^4$$

The numerical values of h and k_0 determined from these are

$$k_0 = 1.526 \times 10^{-16} \text{ ergs per degree}$$
$$h = 7.25 \times 10^{-27} \text{ erg-seconds}$$

Wien's formula is seen to give a value of k_0 about 11 per cent too high.

As to numerical value, if we combine the ratio $h/k_0 = 4.778 \times 10^{-11}$ with the best *experimental* value of k_0, as determined from the gas constant R, namely, $k_0 = 1.372 \times 10^{-16}$, we find, for h,

$$h = 6.555 \times 10^{-27} \text{ erg-second}$$

Birge[1] gives a summary of the values of h determined in various ways and concludes that the most probable value[2] is

$$h = (6.5543 \pm 0.0025) \times 10^{-27} \text{ erg-second}$$

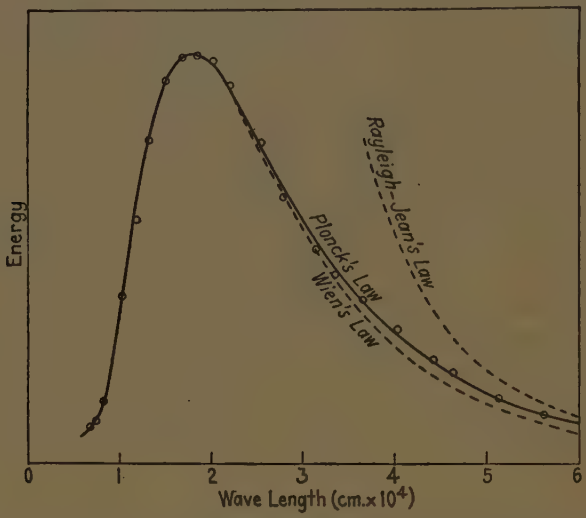

FIG. 65.—Comparison of the three radiation laws with experiment, for the radiation from a black body at 1600°K.

Finally, in Fig. 65 is shown a comparison between the several spectral energy distribution formulæ and experimental data.

[1] *Phys. Rev.*, vol. 14, p. 361 (October, 1919).

[2] It is a curious instance of the mutual cancellation of inaccuracies in numerical data that Planck in his original paper in which he computed the value of h (*Ann. Physik*, vol. 4, p. 563 (1901)) obtained the value 6.55×10^{-27}. He used for the value of $\lambda_m T$ that found by Lummer and Pringsheim a few months before, namely $\lambda_m T = 0.294$ cm deg.; and for the value of a in the Stefan-Boltzmann equation $\psi = aT^4$, $a = 7.061 \times 10^{-15}$ erg. cm.$^{-3}$ deg.$^{-4}$. According to the best of recent measurements this value of $\lambda_m T$ is too high by some 2 per cent; while the value of a is too low by about 7 per cent. But from these data one obtains

$$h = 6.55 \times 10^{-27} \text{ erg-second}$$
$$k_0 = 1.346 \times 10^{-16} \text{ erg-deg.}^{-1}$$

The circles show observations by Coblentz[1] on the energy distribution in the spectrum of a black body at 1600°K. The full line shows the distribution predicted by Planck's formula. The lower dotted line, which coincides with the full line from short wave lengths up to about $\lambda = 2.2\mu$, corresponds to Wien's formula. The upper dotted line is from the Rayleigh-Jeans formula. The superiority of Planck's formula is, at once, evident.

[1] Bull. Bureau of Standards.

CHAPTER VIII

THE QUANTUM THEORY OF SPECIFIC HEATS

We saw in the preceding chapter that the quantum theory originated in an empirical attempt to bring the then current theories of black-body radiation into line with experiment. The attempt was highly successful. But far more striking, and of vastly greater significance, are the successes which the postulate

$$\epsilon = h\nu$$

has had in other branches of physics. Indeed, but for these later successes, it is doubtful whether the theory would have been of much more than secondary importance. For after all, *from the standpoint of agreement with experiment,* the difference between Planck's formula and that of Wien is not so very great, as judged from the graphs in Fig. 65 and the footnote on page 246.

We have already mentioned, in Chap. VI, how the concept of energy quanta seemed to offer the only explanation of the photoelectric effect, the value of the constant h as determined in this way being identical with that obtained in Chap. VII from radiation data. At first glance, there does not seem to be a very close relation between the *observed* phenomena of photoelectricity and those of black-body radiation. But that there must be a very fundamental connection seems to be demonstrated by the identical numerical values of h. Likewise, neither of these phenomena appears to be very closely related to that branch of physics which deals with specific heats. Yet in the field of the specific heats of bodies, the quantum theory had one of its earliest and, in some respects, most astonishing successes. In this chapter, we shall deal very briefly with this aspect of the quantum theory, mainly with the purpose of pointing out, as in Chap. VII, how the newer theory succeeded where the old one partially failed.

1. The Empirical Law of Dulong and Petit.—Over 100 years ago, Dulong and Petit,[1] as a result of the determination of the specific heats of a number of elements such as iron, lead, silver,

[1] *Ann. Chemie et de Physique,* vol. 10, p. 395 (1819).

and gold, concluded that "the product of the atomic weight and the specific heat is the same for all elementary (solid) substances." This law is known as the "law of Dulong and Petit." The product, atomic weight by specific heat, is known as the *atomic heat.*

A few years later, Regnault made an extensive investigation of the specific heats of numerous substances. The mean atomic heat of some 30 solids—excluding some near their melting points—was found to be 6.38 calories per gram-atom per degree.

In 1848, Woestyn[1] extended the law of Dulong and Petit to include molecular heats (*i.e.*, product of molecular weight by specific heat), on the supposition that each atom in a compound has the same thermal capacity as when uncombined.

That the law of Dulong and Petit is approximately true for the atomic heats of many elements in solid form is shown in Table I, compiled from data given in the International Critical Tables:

TABLE I.—ATOMIC HEATS OF VARIOUS ELEMENTS IN THE SOLID STATE

Element	Atomic weight	Melting point, degrees Centigrade	Atomic heat	Temperature, degrees Centigrade
H	1.008	−259	0.57*	−260.6
Li	6.94	186	5.5	0
Be	9.02	1,350	3.85*	0–100
Bo	10.82	2,300	3.35*	0–100
C	12.00	.....	1.45*	20
N	14.01	−210	5.5	−212
Na	23.00	97.5	6.8	20
Al	26.96	660	5.75	20
Si	28.06	1,420	4.95*	20
Cl	35.46	−101	6.7	−113
Ar	39.91	−189	6.2	−223
Fe	55.84	1,535	5.95	20
Zn	65.38	1,700	6.0	0–100
Br	79.29	−7.2	5.6	−150
Rb	85.44	38.5	6.85	0
Mo	96.0	2,620	6.2	20–100
Sn	118.7	232	6.4	18
W	184.0	3,370	6.2	20–100
Au	197.2	1,063	6.15	18
Pb	207.2	327	6.35	20
U	238.2	1,850(?)	6.7	0–100

[1] *Ann. Chemie et de Physique*, vol. 23, p. 295 (1848).

The atomic heat, in calories per gram-atom per degree, is shown in the fourth column. The fifth column gives the temperature at which the measurement was made. Excluding those marked with an asterisk(*), the mean value of the atomic heats given in the table is 6.3 calories per gram-atom per degree, the majority of values being included in the range 5.8 to 6.8. This grouping of atomic heats around the mean value 6.3 is all the more remarkable since the elements shown in the table cover a wide range of properties; *e.g.*, the melting points vary from that of argon (−189°C.) to that of tungsten (+3370°C).

The law of Dulong and Petit can at best, however, be only an approximation, since the departures from the mean value 6.3 are considerably larger than experimental error. Further, the values marked with an asterisk—namely, those for hydrogen, beryllium, boron, carbon, and silicon—are in complete disagreement with the law. These elements, with the exception of hydrogen, are light elements with high melting points.

2. Variation of Atomic Heats of Solids with Temperature.—These exceptions to the law of Dulong and Petit were the subject of extended research, and it was early discovered that at least one reason for the failure of the law in these several cases was the fact that the specific heat varies with temperature. This variation was, indeed, noted by Dulong and Petit themselves as early as 1819. In 1872, Weber[1] observed that the specific heat of diamond (*i.e.*, carbon) increases threefold between 0 and 200°C.

The study of specific heats of substances as a function of temperature has been greatly facilitated in recent years by the availability of liquified gases—liquid air, liquid hydrogen, and liquid helium—for making measurements at low temperatures. It has been found that below a certain temperature characteristic of each substance the specific heats of all solids decrease rapidly with decreasing temperature, reaching a value almost zero even before the temperature of absolute zero is reached. Figure 66 shows the variation with temperature of the atomic heats at constant volume of four characteristic substances: diamond, silicon, aluminum and lead. The data for diamond and silicon are from a paper by A. Magnus;[2] for aluminum and lead, from

[1] *Phil. Mag.*, vol. 44, p. 251 (1872).

[2] A. MAGNUS: *Ann. Physik*, vol. 70, p. 303 (1923).

the work of Nernst and Lindemann, quoted by W. M. C. Lewis.[1] The atomic heat of lead at ordinary (room) temperatures is observed to approximate the value required by the law of Dulong and Petit. But below a temperature of about 100°Abs., the atomic heat of lead drops very rapidly toward zero. The curves for the other three substances have the same general form as that for lead. They differ from lead mainly (1) in the temperature above which they seem to obey the law of Dulong and Petit and (2) in the rate at which the atomic heat decreases below that

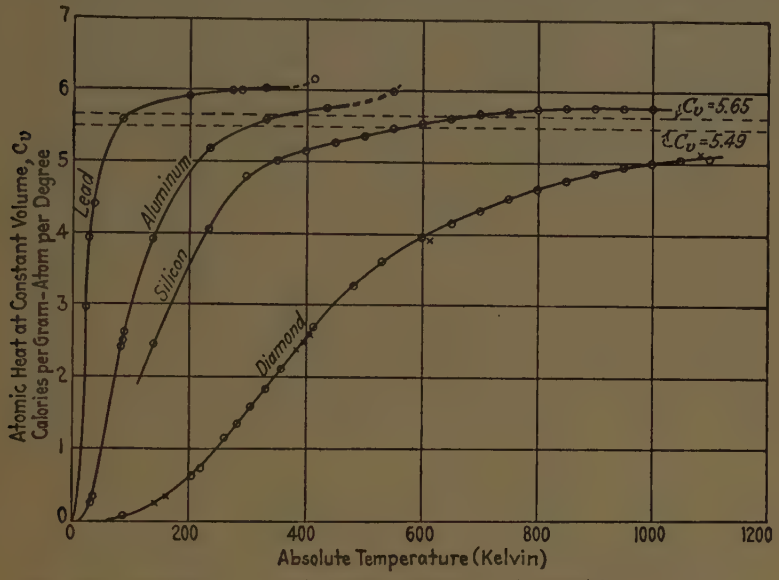

FIG. 66.—Variation of atomic heat at constant volume with temperature.

temperature. In the case of the diamond, the value of (about) 6 calories per gram-atom per degree would not be reached until the temperature exceeded 2000°Abs.

The curves for nearly all substances are similar to those shown in Fig. 66, and they lie between the curves for lead on the one side and for diamond on the other. Indeed, the curves for a large number of elements lie between those for aluminum and for lead. Since most of the measurements on which the law of Dulong and Petit was based were made at *room* temperature, it is obvious, from Fig. 66, why the law is so nearly obeyed.

[1] LEWIS, W. M. C.: "Quantum Theory," 3d ed., p. 68, (1924).

That the curves not only are similar in appearance but also are very closely related to each other by some fundamental underlying law is clearly indicated by the fact that they can be brought (almost) into coincidence by suitable change in the temperature scale for each curve. Thus, if the abscissæ of the curve for aluminum be multiplied by a factor of 4.6, the curve for aluminum will nearly coincide with that for diamond. The crosses (×) on the curve for diamond represent the points from the aluminum curve shifted in this way. What is this fundamental law which governs the variation of specific heat with temperature and which, at sufficiently high temperatures, must give, approximately, the law of Dulong and Petit? Classical physics failed to find the law. The quantum theory was more successful.

3. The Classical Theory of Specific Heats of Solids.—According to the kinetic theory of matter, the atoms of solids execute vibrations about positions of equilibrium with amplitudes which depend on the temperature of the body. With each vibratory atom is associated energy, part kinetic and part potential, the two parts being, on the average, equal, provided the restoring forces are proportional to the displacement so that the vibration of the atom is simple harmonic. If we were to follow the history of any particular atom, we should find that its energy varies greatly from time to time. But its *average* energy over a long period of time would be the same as that of any other atom.

Let us consider an enclosure containing a gas and a small crystalline monatomic solid, all at a temperature T. According to the principle of the equipartition of energy, discussed in Sec. 11 of Chap. VII, each degree of freedom of the solid should have, *on the average*, as much kinetic energy $\bar{E}$ as each degree of freedom of the gas, namely, an amount given by

$$\bar{E} = \tfrac{1}{2}k_0T$$

where k_0 is Boltzmann's constant and T is the absolute temperature. Each atom of the solid has 3 degrees of freedom by virtue of its vibratory motion. It therefore possesses kinetic energy equal to $\tfrac{3}{2}k_0T$. Since with this kinetic energy is associated an equal amount of potential energy, we see that the total average energy per atom of the solid is

$$3k_0T$$

Since a gram-atom of the solid contains N_0 atoms, N_0 being Avogadro's number, it follows that the total thermal energy of agitation W_A of a gram-atom of the solid is

$$W_A = 3k_0N_0T = 3RT \quad (1)$$

since $k_0N_0 = R$, the gas constant.

Now, the specific heat of a substance is equal to the energy required to raise the temperature of 1 gram 1 degree; and, likewise, the atomic heat is equal to the energy required to raise the temperature of 1 gram-atom 1 degree. If, during this rise in temperature, the substance is not allowed to expand, according to the kinetic theory of matter all of this added energy goes to increase the energy of vibration of the atoms. Calling the value of the atomic heat at constant volume C_v, it follows that

$$C_v = \frac{dW_A}{dT} = 3R \quad (2)$$

According to classical theory, then, the atomic heat at constant volume of a monatomic solid should be (1) constant and *independent* of temperature and (2) equal to three times the gas constant R. Since the numerical value of R is 1.987 calories per gram-atom per degree (see p. 219), it follows that the numerical value of C_v, on the classical theory of the equipartition of energy, should be

$$C_v = 5.961 \text{ calories per gram-atom per degree}$$

This is, to a first approximation, the numerical value of atomic heat required by the law of Dulong and Petit. It is close to the value to which the curves in Fig. 66 approach asymptotically as the temperature increases. *But equation* (2) *predicts no variation in atomic heat with temperature, as is required by these experimental curves.*

Suggestions have been made that, perhaps, with decreasing temperature, the number of degrees of freedom get rapidly less, due to groups of atoms becoming "frozen" together. Were this true, the variation of compressibility with temperature should be other than is observed. It appears, therefore, that the classical theory, although predicting approximately the numerical value required by the law of Dulong and Petit, offers no solution to the variation of atomic heat with temperature.[1]

[1] See, however, Compton's theory, p. 275.

Note.—Relation between C_p and C_v.—In general, when bodies, either solids or fluids, are heated, they tend to expand. If, as in the case of a gas, the expansion be prevented by the application of suitable pressure, the energy given to the gas goes to increase the kinetic energy of the molecules. We then have to deal with the atomic heat at constant volume C_v. If, however, the *pressure* be maintained constant, additional energy is required on account of the work, external or internal, or both, which the expanding body does. We then are concerned with the atomic heat at constant pressure C_p. As regards these two specific heats, a solid differs in no way from a gas, except that, in general, the magnitude of the expansion, for a given temperature change, of a solid is much less than the corresponding expansion of a gas.

The specific heat of solids must, in general, be *measured* at constant pressure. The discussion, however, which led to equation (2), namely,

$$C_v = 3R$$

considered *only* the increase in the thermal energy of agitation of the atoms of the solid, no mention being made of external or internal work resulting from heating. Since the experimental values of atomic heats of solids are the atomic heats at *constant pressure* C_p, to compare with experiment the values of C_v, as predicted, either on the classical theory given above or on the quantum theory given below, requires that the *observed* values of atomic heat, *i.e.*, C_p, be reduced to atomic heat at constant volume, *i.e.*, to C_v. This reduction is accomplished by computing the work required to compress the solid *isothermally* back to its original volume at temperature T, after it has been heated from T_1 to T_2. The equation to express the required relation between C_p and C_v takes the form[1]

$$C_p - C_v = \frac{9\alpha^2 MT}{K\rho} \qquad (3)$$

where α is the linear coefficient of expansion; M is the molecular (or the atomic) weight; K is the compressibility; and ρ is the density. Thus, Magnus[2] finds, for diamond,

$$C_p - C_v = 8.00 \times 10^{-6} \times T$$

[1] G. N. LEWIS: (*Journ. Amer. Chem. Soc.*, vol. 29, p. 1165 (1907)), derives a similar equation.

[2] *Loc. cit.*, p. 250.

where the constants in the neighborhood of 50°C. are

$$\alpha = 1.32 \times 10^{-6} \text{ deg.}^{-1}$$
$$K = 0.16 \times 10^{-12} \text{ cm.}^2 \text{ dyne}^{-1}$$
$$\rho = 3.51 \text{ grams cm.}^{-3}$$

For many substances, these constants α, K, and ρ, are not known over the temperature range for which values of C_p are measured. In these cases, use is made of the relation, due to Grüneisen,[1] that at high temperatures the coefficient of expansion α is proportional to C_p, while the product $K\rho$ remains practically constant. Putting

$$\alpha = aC_p$$

and

$$K\rho = B$$

where a and B are experimental constants determined at a temperature at which α, K, and ρ are known, we may write equation (3),

$$C_p - C_v = \frac{9a^2M}{B} C_p^2 T$$
$$= AC_p^2 T$$

where

$$A = \frac{9a^2M}{B} \tag{4}$$

For diamond, $A = 2.64 \times 10^{-6}$, according to Magnus. The constant A is, also, a function of the melting point T_m:

$$A = A_0 \frac{1}{T_m}$$

where A_0, as given by Nernst and Lindemann,[2] is a constant and has the numerical value 0.0214. Table II gives some numerical values of A.

[1] *Ann. Physik*, vol. 26, p. 393 (1908).

[2] See NERNST: "The New Heat Theorem," English translation by G. Barr, p. 65 (1926).

TABLE II.—NUMERICAL VALUES OF A IN $C_p - C_v = AC_p^2T$

Substance	A	Source
Diamond	0.264×10^{-5}	Magnus and Hodler[1]
Boron	0.75	Magnus and Danz[2]
Aluminum	2.2	W. M. C. Lewis[3]
Copper	1.3	W. M. C. Lewis[3]
Lead	3.0	W. M. C. Lewis[3]
Platinum	1.0	W. M. C. Lewis[3]

[1] *Ann. Physik*, vol. 80, p. 818 (1926).
[2] *Ann. Physik*, vol. 81, p. 422 (1926).
[3] Quoted by W. M. C. LEWIS in "Quantum Theory," 3d ed., p. 67.

In Table III is shown the order of magnitude of the difference between C_p and C_v. The difference is small in the case of the diamond but becomes very important for other substances.

TABLE III.—SHOWING THE ORDER OF MAGNITUDE OF THE DIFFERENCE BETWEEN C_p AND C_v FOR SEVERAL SUBSTANCES AT DIFFERENT TEMPERATURES

Substance	T, degrees, absolute	C_p	C_v
Diamond[1]	300	1.522	1.520
	900	4.890	4.833
	1,100	5.137	5.060
Boron[2]	473	3.782	3.731
	873	5.351	5.164
	1,173	5.514	5.252
Copper[3]	87	3.37	3.35
	290	5.75	5.60
	450	6.03	5.81
Lead[3]	23	2.96	2.95
	200	6.12	5.90
	409	6.40	5.94

[1] MAGNUS and HODLER, *loc. cit.*
[2] MAGNUS and DANZ, *loc. cit.*
[3] W. M. C. LEWIS, *loc. cit.*

4. Einstein's Theory of the Atomic Heats of Solids.—(*a*) An important advance in the theory of the specific heats of solids was made by Einstein,[1] who applied the quantum theory to the vibrations of atoms about their positions of equilibrium. Let

[1] *Ann. Physik*, vol. 22, p. 180 (1907).

it be assumed: (1) that the atoms of a monatomic solid vibrate with a frequency ν, the same for all atoms, which depends on the mass of the atom and on the restoring forces brought into play when the atom is displaced; and (2) that these atoms, like Planck's oscillators discussed in Chap. VII, are in equilibrium with ether vibrations of the same frequency and that the average energy U_ν (kinetic plus potential) of each degree of freedom of such vibrations is given by equation (100a), Chap VII.

$$\overline{U}_\nu = \frac{h\nu}{e^{h\nu/k_0T} - 1} \qquad [(100a), \text{Chap. VII}]$$

Since each atom, by virtue of its vibrations, has 3 degrees of freedom, the average energy per atom $\overline{E}_a$ is

$$\overline{E}_a = \frac{3h\nu}{e^{h\nu/k_0T} - 1} \tag{5}$$

and the total energy W_A of the N_0 atoms in a gram-atom is

$$W_A = N_0\overline{E}_a = \frac{3N_0h\nu}{e^{h\nu/k_0T} - 1} \tag{6}$$

As before (equation (2)), the atomic heat at constant volume is obtained by differentiating W_A with respect to T. Therefore,

$$C_v = \frac{dW_A}{dT} = 3N_0h\nu\frac{1}{(e^{h\nu/k_0T} - 1)^2}e^{h\nu/k_0T}\frac{h\nu}{k_0T^2}$$

Multiplying numerator and denominator by k_0, we have, after rearranging and remembering that $N_0k_0 = R$,

$$C_v = 3R\left[\frac{e^{h\nu/k_0T}}{(e^{h\nu/k_0T} - 1)^2}\cdot\left(\frac{h\nu}{k_0T}\right)^2\right] \tag{7}$$

Equation (7) is Einstein's equation, based upon the quantum theory, for the atomic heat of a solid at constant volume. It differs from the equation (2), given by classical theory,

$$C_v = 3R \tag{2}$$

in that the term $3R$ is multiplied by the quantity within the square bracket, which quantity is a function of temperature. According to the quantum theory, therefore, C_v is a function of temperature.

(*b*) *Test of Einstein's Equation.*—The experimental curves shown in Fig. 66 show three main characteristics: (1) At low temperatures, the atomic heat approaches zero; (2) at high temperatures, *i.e.*, sufficiently high for each substance, the atomic heat

approaches 6.0 calories per gram-atom per degree; (3) between these limits, the curves rise rapidly with increasing temperature, approaching the maximum value asymptotically.

Einstein's equation, (7), agrees with experiment as regards the first two of these characteristics: (1) If $T = 0$, the quantity $h\nu/k_0T$ becomes infinite, and it may be readily shown that the square bracket in equation (7) becomes zero. Einstein's equation, therefore, predicts correctly that the atomic heat should become zero at absolute zero. (2) If T becomes very large with

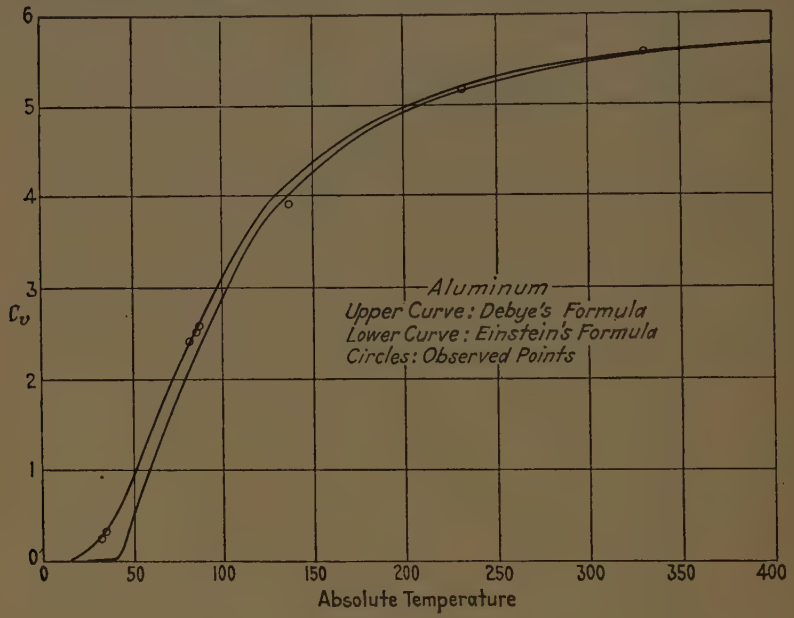

FIG. 67.—Comparison of the specific-heat formulæ of Debye and of Einstein with experiment.

respect to the product $h\nu$, $h\nu/k_0T$ approaches zero, and the square bracket approaches unity. At high temperatures, therefore, the atomic heat should approach $3R$ in agreement with experiment and with the law of Dulong and Petit.

For intermediate temperatures, equation (7) predicts *qualitatively* the variation of atomic heat with temperature but yields too low values at low temperatures. This is shown in Fig. 67, in which the *lower* curve is for the atomic heat of aluminum as given by Einstein's formula,[1] while the circles are the observed

[1] To graph Einstein's formula, it is necessary to determine ν. the characteristic frequency (see Sec. 6, page 260).

values of C_v used in plotting the curve for aluminum, in Fig. 66. In spite of the disagreement, really comparatively small, between theory and experiment, it is quite remarkable that Einstein's theory, based upon the quantum hypothesis, should predict values of C_v so nearly correct. Before considering an improved formula, due to Debye, it will be desirable to comment upon some other consequences of Einstein's equation.

5. Characteristic Temperatures.—If, in the equation (7),

$$C_v = 3R\left[\frac{e^{h\nu/k_0T}}{(e^{h\nu/k_0T} - 1)^2}\left(\frac{h\nu}{k_0T}\right)^2\right] \tag{7}$$

such a value of T be chosen as to make $k_0T = h\nu$, h being Planck's constant and ν being constant, presumably, for a particular substance, the exponent of e becomes unity, and the numerical value of the square bracket becomes 0.921. For this particular value of T, call it T_c, the value of C_v becomes 5.49 (*i.e.*, 5.96×0.921). T_c, as so defined, is a temperature characteristic of the substance and, of course, varies from one substance to another. According to Einstein's theory, we may say that the characteristic temperature T_c of a substance is determined, for any particular substance, *by the temperature at which the atomic heat reaches the value* 5.49. Referring to Fig. 66, the characteristic temperatures may be read directly by observing the points where the horizontal dotted line at the ordinate 5.49 crosses the several curves. These temperatures as read from the curves in Fig. 66 are given in Table IV.

TABLE IV.—CHARACTERISTIC TEMPERATURES AND FREQUENCIES (EINSTEIN)

Substance	T_c, degrees Kelvin	ν sec.$^{-1}$
Lead	78	1.61×10^{12}
Aluminum	307	6.42
Silicon	567	11.9
Diamond[1]	1475	30.8

[1] Extrapolated.

If, *for each substance*, we now define a new temperature scale Θ in which the value of T_c for that substance is the *unit* temperature, the values of the atomic heats of all substances would be the same at *equivalent* points on these scales. Thus, the atomic

heat of lead at $\Theta_{Pb} = 0.5$ (*i.e.*, at 39°K.) should be the same as the atomic heat of silicon at *its* temperature $\Theta_{Si} = 0.5$ (*i.e.*, at 283°K.).

6. Characteristic Frequencies. (*a*) *From Specific Heats.*—From the definition of the characteristic temperature T_c of a substance, we have

$$\frac{h\nu}{k_0 T_c} = 1$$

$$\therefore \nu = \frac{k_0}{h} T_c \tag{8}$$

Knowing the constants h and k_0, and determining T_c, as explained in Sec. 5, *we can compute the value of* ν, *the characteristic frequency with which the atoms of the solid vibrate*, assuming for the moment the correctness of Einstein's equation and its fundamental underlying concepts. The numerical value of the ratio k_0/h is 2.09×10^{10}. The values of ν computed in this way are given in the third column of Table IV.

One now raises the question: Are these values of ν, *computed from the variation of atomic heat with temperature*, values which we may reasonably expect for the frequencies of (thermal) vibration of the atoms of crystalline solids? As to magnitude, they are seen to be of the order of one one-hundredth of the frequencies of light vibrations in the visible part of the spectrum. The following independent methods for determining these frequencies in solids lead to values in substantial agreement with those computed from specific-heat data.

(*b*) *From the "Reststrahlen."*—One of the most instructive, and one of the most convincing, of these methods is that due to Rubens[1] and collaborators, in which they used the phenomenon of selective reflection for isolating long waves. The reflectivity[2] R of a substance for radiation of wave length λ depends on both the coefficient of absorption[3] of the substance and its refractive index n at that wave length, the value of R being given by

$$R = \frac{(1-n)^2 + n^2\kappa^2}{(1+n)^2 + n^2\kappa^2} \tag{9}$$

[1] RUBENS and NICHOLS: *Ann. Physik*, vol. 60, p. 418 (1897); RUBENS and KURLBAUM: *Ann. Physik*, vol. 4, p. 649 (1901); RUBENS and HOLLNAGEL: *Phil. Mag.*, vol. 19, p. 761 (1910); RUBENS and VON WARTENBERG: *Sitzb. d. königl. preuss. Akad.*, p. 169, 1914.

[2] For definition, see Chap. VIII, Sec. 2 (*e*).

[3] Not "absorptivity" (see p. 186).

where κ is a quantity which is known as the "extinction coefficient" and which is closely related[1] to the coefficient of absorption μ, defined on page 186. Any substance which exhibits *selective* absorption in any spectral region presumably has resonating mechanisms whose natural periods coincide with the central part of the absorption band. In those regions, the value of κ and, therefore, of $n\kappa$ may become large enough compared to $(n - 1)$ to raise the value of the reflectivity R considerably above its value for neighboring spectral regions. The substance then exhibits *selective* reflection. Confirmation of this relation between *selective* absorption and *selective* reflection is found in the work of Nichols and of Rubens on quartz. Quartz is transparent, or nearly so, up to about 7.5μ but has a very strong absorption band (really, two bands near together) at about 8.5μ. At 8.5μ, quartz is found to reflect 80 per cent, while, at 4μ, where it is quite transparent, it reflects only a few per cent.

[1] If a beam of light of wave length λ and intensity I_0 passes through a thin slab of absorbing material of thickness d, the intensity I on emerging is given by

$$I = I_0 e^{\frac{-4\pi\kappa}{\lambda} d}$$

where κ is the extinction coefficient. Let the thickness of an absorbing layer be equal to λ so that $d/\lambda = 1$. Then

$$I_1 = I_0 e^{-4\pi\kappa}$$

where I_1 is the emergent intensity after passing a thickness equal to *one* wave length. We may then write

$$\log_e \frac{I_0}{I_1} = 4\pi\kappa$$

or

$$\kappa = \frac{1}{4\pi} \log_e \frac{I_0}{I_1}$$

Unless the substance is so strongly absorbent that the ratio I_0/I_1 is appreciable, κ is a very small quantity, and may be neglected in computing R by equation (9). Thus for glass for which $n\kappa << (1 - n)$, at least in the visible region, $R = \dfrac{(1 - n)^2}{(1 + n)^2}$. But for most metals in the visible region of the spectrum κ may be considerably larger than n. Thus Drude ("Theory of Optics") gives the product $n\kappa$ for platinum as 4.26, while the value of n is 2.06. These values, put in equation (9), give for the reflecting power of platinum about 0.70. Hagen and Rubens (*Ann. Physik*, vol. 1, p. 352 (1900)) found the reflecting power of platinum, at $\lambda = 0.65\mu$, to be 0.66.

A derivation of equation (9) may be found in Wood's "Physical Optics" or in any textbook on the electromagnetic theory of light.

Conversely, if a substance is found to exhibit selective reflection in any region, the substance must have resonators whose natural frequency coincides nearly[1] with the frequencies which are selectively reflected. If a continuous spectrum be reflected from a substance which shows selective reflection at a wave length λ_0, the reflected beam will be relatively much richer in radiation of that wave length than was the incident beam. After several such reflections, the radiation may be comprised almost entirely of the wave lengths which are selectively reflected, the remainder having been almost completely absorbed. The radiation remaining after several such reflections is called "residual rays" or "reststrahlen."

By this method of "reststrahlen," Rubens and his collaborators succeeded in isolating the residual rays from a number of substances. Some of their results are shown in the second and third columns of Table V. For purposes of comparison, there is

TABLE V.—RESIDUAL RAYS FROM CERTAIN SOLIDS

Substance	Wave length	Frequency, sec.$^{-1}$	Computed from Einstein's formula		Computed from the Nernst-Lindemann formula, frequency, sec.$^{-1}$
			T_c	Frequency, sec.$^{-1}$	
NaCl	52.0μ	5.77×10^{12}	220	4.60×10^{12}	5.55×10^{12}
KCl	63.4	4.73	175	3.66	4.55
KBr	82.6	3.64	155	3.24	3.87
KI	91.4	3.28			
$CaCO_3$	98.7	3.04			
AgBr	112.7	2.66			

given, in the fifth column, for the three substances NaCl, KCl, and KBr, the frequency determined by the specific-heat method (Einstein's formula), *viz.*: From data quoted by Lewis[2] the atomic heat was plotted as a function of temperature, and the value of T_c was determined in the same way as in Fig. 66 and Table IV. These values of T_c are given in the fourth column of Table V. The frequency ν was then computed by equation (8).

[1] "Nearly," because R depends not only on κ but on n, and n varies rapidly in the neighborhood of an absorption band.

[2] "Quantum Theory," 3d. edition, p. 70.

While the agreement in these three cases is not quantitative within the limit of error of experiment, it is excellent as far as concerns order of magnitude and relative values from one substance to another. The corresponding frequencies, computed from the Nernst-Lindemann formula, to which reference will be made later, are given in the last column. These are seen to be in excellent agreement with the values obtained by the method of reststrahlen, which method comes as near as one could wish to a *direct* method of observing the frequencies of atomic vibrations in solids.

(*c*) *From Compressibilities.*—Besides this method of determining the frequency, based on Einstein's formula, or on the Nernst-Lindemann formula, there are several indirect methods which give reasonably concordant results. Einstein[1] has derived a relation which makes it possible to compute the frequency of the atomic vibrations from the compressibility K, the atomic weight A, and the atomic volume V_A of the substance. The following are the underlying principles of this method: Solids are, with few exceptions, crystalline—a concept abundantly confirmed by X-ray analysis. In each crystal, the atoms are arranged in a regular "lattice," each atom being held in a position of equilibrium by forces of some kind due to the presence of neighboring atoms. These forces are the same on each atom throughout the entire crystal. They must, also, be intimately connected with the compressibility of the crystal; the greater these forces the *less* the compressibility. Let the mass of an atom be m and the force per unit displacement acting on it when displaced from its equilibrium position be f_0. Then, according to the ordinary laws of mechanics, we should have the period of vibration T of the atom given by

$$T = 2\pi \sqrt{\frac{m}{f_0}} \tag{10}$$

if the return force be proportional to the displacement. The frequency of vibration is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f_0}{m}} \tag{11}$$

The compressibility is defined as the "fractional *decrease* in volume per unit *increase* in (applied) pressure." The compressibility should be (1) greater the less f_0 and (2) greater the greater

[1] *Ann. Physik*, vol. 34, pp. 170, 590 (1911).

the average distance d between the atoms of the crystal. It is reasonable to assume—although a rigorous proof would have to justify the assumptions—that

$$1.\ K \propto \frac{1}{f_0}$$

$$2.\ K \propto d$$

or,

$$K = C\frac{d}{f_0} \tag{12}$$

where C is a proportionately constant. If V_A is the volume of a gram-atom, and if we assume a regular arrangement of the atoms of the crystal, we may determine d by

$$d = \sqrt[3]{\frac{V_A}{N_0}} \tag{13}$$

when N_0 is Avogadro's number. Putting this value of d into equation (12) and solving for f_0, we have

$$f_0 = \frac{C}{K}\sqrt[3]{\frac{V_A}{N_0}} \tag{14}$$

We then have, for the frequency ν, by equations (11) and (14),

$$\nu = \frac{\sqrt{C}}{2\pi}\sqrt[6]{\frac{V_A}{K^3 m^3 N_0}} \tag{15}$$

$$= \frac{\sqrt{C}\ \sqrt[3]{N_0}}{2\pi}\sqrt[6]{\frac{V_A}{K^3 A^3}}$$

$$= C'\sqrt[6]{\frac{V_A}{K^3 A^3}} \tag{16}$$

by multiplying numerator and denominator under the radical by N_0^2 and remembering that $A = mN_0$ where A is the atomic weight. Einstein evaluates the constant C by considering the lattice array of atoms. He found the numerical value of C' to be 2.8×10^7. This gives

$$\nu = 2.8 \times 10^7 \cdot \sqrt[6]{\frac{V_A}{K^3 A^3}} \tag{17}$$

which is one form of Einstein's equation for the atomic frequencies based on compressibilities. Some values of frequency determined by Einstein in this way are given in Table VI.

TABLE VI.—SOME OF EINSTEIN'S VALUES OF ν FROM COMPRESSIBILITIES

Substance	Frequency, sec.$^{-1}$
Al	6.6×10^{12}
Cu	5.7
Pt	4.6
Au	3.8
Pb	2.2
Bi	1.8

The values for aluminum and lead are seen to compare favorably with those given in Table IV.

(*d*) *From Melting Points.*—This method of computing frequencies is due to Lindemann.[1] It is based on the assumption that the melting point T_m of a solid is the temperature at which the amplitude of vibration of the atoms is equal to ("of the same order of magnitude as" would be preferable) the average distance apart d of the atoms. We can determine the way in which the several quantities enter into Lindemann's formula as follows:

As before (equation (11)), let

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f_0}{m}} \tag{11}$$

where ν is the frequency, f_0 is the restoring force per unit displacement of the atom, and m is its mass. If the amplitude of vibration is d, the potential energy at maximum displacement is $\frac{1}{2} f_0 d^2$. This is, also, the (time) average $\bar{E}_d$ of the energy of the atom for the amplitude d. Therefore,

$$\bar{E}_d = \tfrac{1}{2} f_0 d^2$$

$$\therefore f_0 = \frac{2\bar{E}_d}{d^2} \tag{18}$$

Putting this value of f_0 into equation (11) and solving for $\bar{E}_d$ gives

$$\bar{E}_d = 2\pi^2 \nu^2 m d^2 \tag{19}$$

Now, the melting point T_m is usually much higher than the characteristic temperature T_c, so that the energy of an atom due to its vibratory motion at temperature T_m is given by the classical value $3k_0T_m$. Therefore,

$$2\pi^2 \nu^2 m d^2 = 3k_0 T_m \tag{20}$$

[1] *Phys. Zeitsch.*, vol. 11, p. 609 (1910).

As before (equation (13)), let

$$d = \sqrt[3]{\frac{V_A}{N_0}} \qquad [13]$$

where V_A is the volume of a gram-atom at temperature T_m. We now have a value of ν from equation (20), given by

$$\nu = \frac{1}{\pi}\sqrt{\frac{3k_0}{2}}\sqrt[3]{\frac{T_m^{3/2} N_0}{m^{3/2} V_A}}$$

Since $A = mN_0$ ($A \equiv$ atomic weight), we have, finally, for ν,

$$\nu = \left[\frac{1}{\pi}\sqrt{\frac{3k_0}{2}} N_0^{5/6}\right] \cdot \sqrt{\frac{T_m}{A V_A^{2/3}}} \qquad (21)$$

The quantities within the square bracket are all constant, so that the equation for ν is of the form

$$\nu = C\sqrt{\frac{T_m}{A V_A^{2/3}}} \qquad (22)$$

C is, however, determined from comparison with experiment rather than from k_0 and N_0. The equation (22) is, therefore, of value only in determining the way in which the frequency depends on the melting point T_m, the atomic weight A, and the atomic volume V_A at the melting point. C is found to be of the order of magnitude of 2.8×10^{12}. Some values of ν computed by Nernst and Lindemann from this formula are given in the following table:

FREQUENCY BY LINDEMANN'S "MELTING-POINT" FORMULA

Substance	T_m, degrees Kelvin	ν, sec.$^{-1}$
Al	930	7.6×10^{12}
Cu	1,357	6.8
Diamond	3,600(?)	32.5
Pb	600	1.8

(*e*) These several methods of determining the frequency of vibration of the atoms of solids, although differing widely, yield values so nearly in accord with each other as to leave little doubt that the general underlying principles are, in each case, substantially correct. The first method (using Einstein's specific-heat formula) is based on the quantum theory as introduced by

Planck. The others (using, respectively, the reststrahlen, compressibilities, and melting points) are quite independent of the quantum theory.

Biltz,[1] by use of the melting-point formula of Lindemann, has computed the frequencies of a large number of the elements in the solid state and finds that the frequencies are periodic functions of atomic weight.

7. The Nernst-Lindemann Formula for Atomic Heats.—It was pointed out in Sec. 4 (Fig. 67) that Einstein's formula (equation (7)) predicts values of specific heat which are considerably too low at low temperatures. Nernst and Lindemann[2] proposed an empirical modification of Einstein's expression, which was based upon the assumptions (1) that there are *two*, instead of one, characteristic frequencies in a solid, namely, a frequency ν and its first lower octave $\nu/2$; and (2) that one half of the atoms vibrate with the one frequency and the other half with the other frequency. Applying Einstein's formula to each group of atoms the total atomic heat C_v becomes

$$C_v = \frac{3}{2}R\left[\frac{e^{h\nu/k_0T}}{(e^{h\nu/k_0T}-1)^2}\left(\frac{h\nu}{k_0T}\right)^2 + \frac{e^{h\nu/2k_0T}}{(e^{h\nu/2k_0T}-1)^2}\left(\frac{h\nu}{2k_0T}\right)^2\right] \quad (23)$$

The assumptions on which the formula is based can hardly be justified, yet the formula agrees remarkably well with experiment. In Table VII are shown the observed values of the atomic heat of aluminum (quoted by LEWIS, Quantum Theory, p. 68)

TABLE VII.—COMPARISON OF THE NERNST-LINDEMANN AND OF THE EINSTEIN FORMULAS WITH EXPERIMENT. C_v OF ALUMINUM.

Temperature, degrees Kelvin	C_v observed	C_v computed	
		Nernst-Lindemann	Einstein
32.4	0.25	0.22	0.03
35.1	0.33	0.32	0.05
83.0	2.41	2.40	2.12
86.0	2.51	2.51	2.26
137	3.91	3.99	3.98
285	5.17	5.14	5.17
331	5.58	5.51	5.54
555	5.98	5.79	5.81

[1] Quoted in LEWIS: "Quantum Theory," 3d ed., p. 63.

[2] *Sitz. d. königl. preuss Akad.*, p. 494 (1911).

and those computed by the Nernst-Lindemann formula, together with, for comparison, the values predicted by Einstein's formula.

In spite of the superiority of the Nernst-Lindemann formula, its empirical nature robs it of much of its importance. It does, however, call attention to a very important point in connection with the quantum theory of specific heats. Einstein's equation presupposes a *single* frequency characteristic of each solid, an assumption which is hardly tenable, even in the case of monatomic solids, and is inadmissable in the case of such diatomic compounds as NaCl, KBr, etc. That the Nernst-Lindemann formula is more successful by assuming *two* frequencies suggests the direction in which improvement in theory may be expected. This extension was made by Debye.

8. Debye's Theory of Atomic Heats.[1]—(*a*) Let us postulate, for the moment, a solid the molecules of which have no thermal vibrations but are at rest in their respective positions of equilibrium. Now, let a system of standing waves, say longitudinal, be set up in the solid. Each atom is now vibrating with an amplitude which depends on the position of the atom with respect to the nodes and loops of the wave system. If we superpose more and more standing-wave systems of both the same frequency as the original and of different frequencies, the vibrations of any particular atom become more and more complex, until, finally, we may approach a condition of atomic agitation similar to the temperature vibrations. Conversely, we may think of the temperature vibrations of the atoms of a solid as being the equivalent of a vast complex of standing waves of a great range of frequencies. The range of frequencies, however, does not extend from zero to infinity. The lower limit to the frequency is the "fundamental" frequency of the solid—just as in the case of a violin string or an organ pipe. The highest frequency is the frequency of the shortest waves which the solid can transmit. These latter wave lengths are of the order of magnitude of the distance between atoms.

In elastic solids, two distinct systems of waves are recognized: (1) longitudinal waves, velocity v_L and (2) transverse waves, velocity v_T. These velocities are determined by the elastic constants of the material and its density.

We may think of these standing-wave systems, just as in the case of ether waves, as making up a great number of degrees of

[1] *Ann. Physik*, vol. 39, p. 789 (1912).

freedom. In Chap. VII, Sec. 13, we discussed the number of such degrees of freedom per unit volume. We showed that the number of degrees of freedom per unit volume $d\phi_L$ of longitudinal waves in the wave-length range λ to $\lambda + d\lambda$ is (see equation (85), Chap. VII)

$$d\phi_L = 4\pi \frac{d\lambda}{\lambda^4}$$

and for transverse waves (see equation (86), Chap. VII),

$$d\phi_T = 8\pi \frac{d\lambda}{\lambda^4}$$

Changing wave length λ to frequency ν by the relations $\lambda = v/\nu$ and $d\lambda = (v/\nu^2)d\nu$, these equations become

$$d\phi_L = 4\pi \frac{\nu^2}{v_L^3} d\nu$$

$$d\phi_T = 8\pi \frac{\nu^2}{v_T^3} d\nu$$

The total number of degrees of freedom $d\phi$ in unit volumes of the solid in the frequency range ν to $\nu + d\nu$ is the sum $(d\phi_L + d\phi_T)$, since both systems of waves are *simultaneously* present. Therefore,

$$d\phi = d\phi_L + d\phi_T = 4\pi \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \nu^2 d\nu \tag{24}$$

(*b*) Now, let us assume that with each of these degrees of freedom of frequency ν is associated an average amount of energy $\overline{U}_\nu$ (see equation (100), Chap. VII, where $\epsilon = h\nu$) equal to

$$\overline{U}_\nu = \frac{h\nu}{e^{h\nu/k_0 T} - 1}$$

The energy dW_A in all the degrees of freedom in this frequency range ν to $\nu + d\nu$ in a volume V_A equal to the volume of a gram-atom is

$$\begin{aligned} dW_A &= V_A \overline{U}_\nu d\phi \\ &= 4\pi V_A \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{h\nu}{e^{h\nu/k_0 T} - 1} \nu^2 d\nu \end{aligned} \tag{25}$$

The total energy W_A of the gram-atom, taking into account all frequencies, is

$$W_A = \int dW_A = 4\pi V_A \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \int_0^{\nu_m} \frac{h\nu}{e^{h\nu/k_0 T} - 1} \nu^2 d\nu \tag{26}$$

In this integration, the lower limit is zero, since the fundamental frequency of any solid of experimental dimensions is very small, practically zero. The upper limit ν_m is the maximum frequency of vibration which the solid is capable of transmitting. This frequency is assumed to be of the order of magnitude of the natural frequency of the atoms as determined by, say, the Lindemann melting-point formula.

The total number of degrees of freedom ϕ in the gram-atom must be the same whether we compute ϕ by integration, within proper limits, of equation (24) or assign to each of the N_0 atoms 3 degrees of freedom. Therefore,

$$3N_0 = 4\pi V_A\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\int_0^{\nu_m}\nu^2 d\nu = \frac{4\pi V_A}{3}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\nu_m^3 \qquad (27)$$

$$\therefore \frac{9N_0}{\nu_m^3} = 4\pi V_A\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right) \qquad (28)$$

Since the velocities are computable from the elastic constants, equation (28) makes it possible to compute ν_m. Better values of C_v, however, are obtained[1] in the formula for C_v derived below (*i.e.*, equation (35)) by computing ν_m from Lindemann's melting-point formula (equation (22)).

By use of equations (27) and (28), we may now write for W_A, in equation (26),

$$W_A = \frac{9N_0}{\nu_m^3}\int_0^{\nu_m}\frac{h\nu}{e^{h\nu/k_0T}-1}\nu^2 d\nu \qquad (29)$$

(This equation in Debye's theory corresponds to equation (6) in Einstein's theory.)

To obtain the atomic heat at constant volume C_v, we wish to compute from equation (29) the value of dW_A/dT. This derivative is usually, and more easily, obtained by a change of variables, *viz.*: Let us define the characteristic temperature T_c in Debye's theory in a manner similar to that followed in Einstein's theory (sec. 5) by the relation

$$T_c = \frac{h\nu_m}{k_0} \qquad (30)$$

ν_m being the *maximum* frequency. Also, put

$$x \equiv \frac{h\nu}{k_0T}$$

$$\therefore d\nu = \frac{k_0T}{h}dx \qquad (31)$$

[1] LEWIS: "Quantum Theory," 3d ed., p. 330.

The necessary changes in limits are

$$\text{when } \nu = 0,\ x = 0$$

$$\text{when } \nu = \nu_m;\quad x = x_m = \frac{h\nu_m}{k_0 T} = \frac{T_c}{T} \tag{32}$$

With these changes in the variable from ν to x, we rewrite equation (29),

$$W_A = 9N_0k_0\frac{T^4}{T_c^3}\int_0^{T_c/T}\frac{x^3}{e^x - 1}dx \tag{33}$$

We may now compute C_v:

$$C_v = \frac{dW_A}{dT} = 9N_0k_0\left[4\frac{T^3}{T_c^3}\int_0^{T_c/T}\frac{x^3}{e^x - 1}dx - \frac{T^4}{T_c^3}\int_0^{T_c/T}\left(\frac{3x^2}{e^x - 1} - \frac{x^3e^x}{(e^x - 1)^2}\right)\frac{x}{T}dx\right] \tag{34}$$

The second integral at once becomes, after integration,

$$\frac{T^3}{T_c^3}\left[\frac{x^4}{e^x - 1}\right]_0^{T_c/T}$$

After substituting the limits in this integral, we finally have, for C_v,

$$C_v = 9N_0k_0\left[4\left(\frac{T}{T_c}\right)^3\int_0^{T_c/T}\frac{x^3}{e^x - 1}dx - \frac{T_c}{T}\frac{1}{e^{T_c/T} - 1}\right] \tag{35}$$

This is Debye's equation for the specific heat of a solid at constant volume.

(*c*) *Test of Debye's Equation.*—(1) At high temperatures Debye's equation should yield the classical value of C_v, namely, $3N_0k_0$ or $3R$. For large values of T, x becomes small, and T_c/T becomes small. Since $e^x = 1 + x + \cdots$, in which expansion for small values of x we may drop x^2 and higher terms, we have, for high temperatures,

$$\left.\begin{aligned} &1.\ \frac{T_c}{T}\cdot\frac{1}{e^{T_c/T} - 1} = 1 \\ &2.\ 4\left(\frac{T}{T_c}\right)^3\int_0^{T_c/T}\frac{x^3}{e^x - 1}dx = 4\left(\frac{T}{T_c}\right)^3\int_0^{T_c/T}x^2dx = \frac{4}{3} \end{aligned}\right\} \tag{36}$$

$$\therefore C_v = 9N_0k_0(\tfrac{4}{3} - 1)$$
$$= 3N_0k_0 = 3R$$

This is in agreement with the law of Dulong and Petit and with experiment.

(2) At low temperatures, x and T_c/T are both large. The second term in the square bracket of equation (35) vanishes. The integral, now taken between the limits 0 and ∞, becomes[1]

$$6\left(1+\frac{1}{2^4}+\frac{1}{3^4}+\cdots\right).$$

Therefore, since

$$\left(1+\frac{1}{2^4}+\frac{1}{3^4}+\cdots\right)=1.082$$

$$C_v = 9N_0k_0\left[4\left(\frac{T}{T_c}\right)^3\times 6\cdot 1.082\right]$$

$$= \frac{234N_0k_0}{T_c^3}T^3$$

$$= (\text{constant})\times T^3 \qquad (37)$$

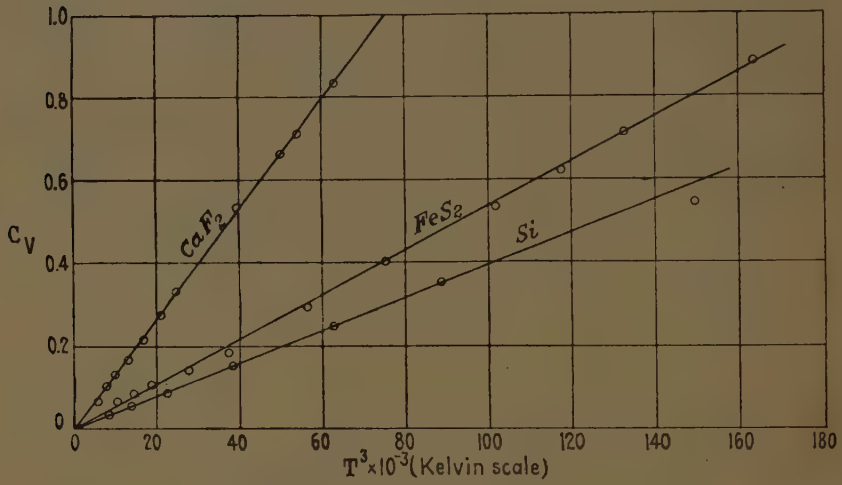

FIG. 68.—At low temperatures, the molecular heat at constant volume is proportional to the cube of the absolute temperature.

At low temperatures, therefore, the atomic heat of a solid should be proportional to the *cube* of the absolute temperature. This is confirmed by experiment over a considerable range of temperatures. Schroedinger[2] quotes extensive data bearing on this point, curves for several of the substances given in his table being shown graphically in Fig. 68, where C_v is plotted against the cube of the absolute temperature for CaF_2 (17 to 40°K.), FeS_2 (22 to

[1] See a similar evaluation on p. 244.

[2] *Phys. Zeitsch.*, vol. 20, p. 498 (1919).

57°K.), and Si (20 to 53°K.). The proportionality is seen to hold from almost vanishingly small values of C_v, well up toward $C_v = 1$. Beyond this point, as theory requires, the curves become increasingly convex toward the T^3-axis.

(3) For intermediate temperatures, it is necessary to evaluate Debye's formula by the summation of series.[1] These computations are now available in the form of tables[2] which give C_v as a function of T_c/T. The upper curve of Fig. 67 is the graph of Debye's formula for aluminum, taking $T_c = 398$. The agreement between the graph and the observations is seen to be excellent.[3]

(4) From equation (28), the maximum frequency ν_m should be given by

$$\nu_m^3 = \frac{9N_0}{4\pi V_A\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)} \tag{38}$$

It is possible to compute the velocities v_L and v_T from the elastic constants of the solid. H. S. Allen[4] has calculated ν_m in this way for a number of elements, several of which are given here:

ELEMENT	ν_m
Al	8.26×10^{12} sec.$^{-1}$
Cu	6.81
Ag	4.39
Au	3.44
Pb	1.49

There is reasonably good agreement between these values and those found by other methods.

In short, Debye's theory of atomic heats is in excellent agreement with experiment over a very wide temperature range.

9. Further Considerations.—Excellent as it is in so far as agreement with experiment is concerned, Debye's theory is by no means the "last word" in the theory of atomic heats. For a more detailed discussion, the reader is referred to more extensive treatises on the quantum theory. Here we can make brief reference only to two or three further considerations.

[1] For details see Debye's paper *loc. cit.*: *Ann. Physik*, vol. 39, p. 789 (1912).

[2] NERNST: "The New Heat Theorem," pp. 246–254.

[3] LEWIS' "Quantum Theory" gives numerous tables showing agreement between observed values of C_v and those computed from Debye's formula.

[4] *Proc. Roy. Soc.*, vol. 94, p. 100 (1917).

(*a*) *The Theory of Born and Karman.*[1]—This theory, developed by Born and Karman, simultaneously with, but independent of, the theory of Debye, differs from Debye's theory in that the number of free vibrations in a crystalline solid is computed by considering the arrangement of the atoms of the crystal in a space lattice or in an interpenetrating series of such lattices. Although the theory meets several formal objections inherent in Debye's theory, the resulting formulæ and their interpretation are much more complex than those of Debye and are, therefore, quite beyond the scope of an elementary text.

(*b*) *Specific Heats of Very Low Temperatures.*—Schaefer[2] points out that below a certain frequency ν_p it is inadmissible to compute frequencies by integration from *zero* as a lower limit, as was done in equation (27), since in this region of very low frequencies the "distribution" of frequencies is not sufficiently continuous. Rather, from the fundamental frequency (or from zero frequency) up to some frequency ν_p, one must use a *summation* rather than an integration. From ν_p up to ν_m, the integral is applicable. The result of this formal change is of importance only at very low temperatures. Schaefer concludes that there is for each substance a very low temperature T_0 below which Debye's T^3 law does not hold. From absolute zero up to T_0, the variation of C_v with temperature should follow an exponential law.

(*c*) *Specific Heats at Very High Temperatures.*—The several formulæ discussed above approach asymptotically at high temperatures the classical value $C_v = 3R = 5.961$ calories per gram-atom per degree. It has long been known, however, that at very high temperatures the atomic heat considerably exceeds this value. The atomic heat of Fe at 1200°C. is 9.6; of Sn at 1100°C., 9.2; of copper at 900°C., 7.1. Magnus and Danz[3] find that the atomic heat of tungsten increases linearly from 7.092 at 400°C. to 7.506 at 900°C. These high values are explained by assuming that with higher temperatures an increasing number of degrees of freedom come into play. If any atomic vibrating mechanism in any system has a natural frequency ν_i, the quantum of energy for which is $h\nu_i$, that mechanism will, in general, not possess its full average quota of energy

[1] REICHE: "The Quantum Theory," English translation, pp. 42–58.
[2] *Zeit. für. Physik*, vol. 7, p. 287 (1921).
[3] *Ann. Physik*, vol. 81, p. 407 (1926).

unless the average energy per degree of freedom of the system with which the mechanism is associated equals or exceeds $h\nu_i$. Taking the classical value of k_0T as the energy per vibration (the quantum theory is in agreement with this at high temperatures), the temperature of the system below which the frequency ν_i will be "partially suppressed" is determined by

$$k_0T = h\nu_i$$

When the temperature approaches or exceeds this limit the degrees of freedom of this frequency ν_i become increasingly active; the total number of degrees of freedom of the system increase; and, accordingly, the specific heat increases. It is reasonable to assume that these additional degrees of freedom which become active at high temperatures in solids are due to electrons, which, in part because of their small mass, have higher frequencies than the atoms.

(*d*) *Extension of the Classical Theory.*—In Sec. 3, it was shown that the value of the atomic heat of solids demanded by the classical theory is $3R$, independent of temperature. It has, however, been shown by A. H. Compton,[1] for the region of lower temperatures, and by Adams,[2] for the region of higher temperatures, that formulæ can be developed without the aid of the quantum theory and by use of very reasonable assumptions, which are in good agreement with experiment.

Compton assumes that

> . . . if the relative energy between two neighboring atoms in a solid falls below a certain critical value, the two atoms become "agglomerated" so that the degree of freedom between them vanishes; but as soon as the energy increases again above the critical value the degree of freedom reappears.

This means that as, with decreasing temperature, the thermal agitation becomes less, more and more degrees of freedom vanish and the atomic heat becomes less. From this postulate, Compton deduces an equation for C_v:

$$C_v = 3N_0k_0\,e^{-T_c/T}\left(\frac{T_c}{T} + 1\right) \tag{39}$$

[1] *Phys. Rev.*, vol. 6, p. 377 (1915).

[2] ADAMS, E. P.: "The Quantum Theory," *Nat. Research Council, Bull.*, vol. 7, part 3 (November, 1923).

T_c is, as in the other theories, a "characteristic" temperature defined by the equation

$$T_c = \frac{\epsilon}{2k_0}$$

where ϵ is "the critical value of the energy below which a degree of freedom remains agglomerated." This characteristic temperature in Compton's theory is the temperature at which[1]

$$C_v = 3N_0k_0\frac{2}{2.71} = 4.40$$

Several such temperatures, determined by Compton are as follows:

SUBSTANCE	T_c, DEGREES KELVIN
Diamond	794
Cu	133
Al	170
Pb	38.4

Compton's formula agrees well with experiment, as Table VIII, taken from his paper, shows.

TABLE VIII.—ATOMIC HEAT BY COMPTON'S FORMULA

T, (degrees Kelvin)	C_v, (observed)	C_v, (calculated)	T, (degrees Kelvin)	C_v, (observed)	C_v, (calculated)
Diamond			Aluminum		
88	0.03	0.01	32.4	0.25	0.19
205	0.62	0.63	83	2.40	2.40
222	0.76	0.80	137	3.91	3.94
306	1.58	1.60	235	5.17	5.09
413	2.64	2.62	331	5.58	5.55
1169	5.24	5.18	555	5.98	5.85
Copper			Lead		
23.5	0.22	0.14	23.0	2.95	3.04
33.4	0.54	0.56	28.3	3.91	3.69
88	3.37	3.36	36.8	4.38	4.38
137	4.53	4.54	38.1	4.43	4.45
290	5.66	5.60	90.2	5.63	5.67
450	5.87	5.86	200	5.91	5.98

[1] Put $T = T_c$ in equation (39).

In a critical comparison of the predictions of Compton's formula with experimental results, however, F. Schwers[1] concludes that at very low temperatures Compton's formula gives too low values of C_v; that Debye's formula is much superior. This is shown by Table IX, for the specific heat of aluminum, taken from Schwers' paper.

TABLE IX.—COMPARISON OF THE FORMULAE OF DEBYE AND OF COMPTON WITH EXPERIMENT

Temperature, degrees Kelvin	C_v observed	C_v computed	
		Debye: $T_c = 382$	Compton: $T_c = 164$
19.1	0.066	0.058	0.010
23.6	0.110	0.109	0.045
27.2	0.162	0.166	0.101
33.5	0.301	0.310	0.260
37.1	0.396	0.409	0.390
41.9	0.597	0.613	0.586
49.6	0.901	0.907	0.939
53.4	1.105	1.084	1.126
62.4	1.543	1.520	1.561
73.4	2.070	2.060	2.077
79.1	2.345	2.362	2.303

Adams[2], by the methods of classical statistical mechanics, finds that at high temperatures C_v should be a linear function of T, *viz.*,

$$C_v = 3N_0k_0(1 + \alpha k_0 T) \tag{40}$$

where α is a constant (*independent* of the quantum constant h and *not* empirical). Adams shows that this same formula may also be derived from quantum-theory considerations. Equation (40) is seen to be in agreement with the data on tungsten given by Magnus and Danz[3], in so far as the linear variation of C_v with temperature is concerned.

That equation (40) is obtainable on the basis of either the classical or the quantum theory is, perhaps, only an *extension* of the agreement between the two theories in predicting the value $3R$

[1] *Phys. Rev.*, vol. 8, p. 117 (1916).
[2] *Loc. cit.*
[3] *Loc. cit.*, p. 274.

for the specific heat at (moderately) high temperatures. The difference between the two methods of deriving the equation lies in the fundamental concepts involved. Perhaps we shall ultimately come to understand that even these fundamental concepts are in harmony with each other.

10. The Atomic Heat of Gases. (*a*) *Classical Theory.*—The problem of the specific heats of gases is somewhat more complex than the corresponding problem for solids. The atoms of the latter have freedom of motion in respect of vibration only. The atoms of a gas, however, have, in general, at least three types of motion—translation, rotation, and, for polyatomic gases, vibration of the atoms of the molecule with respect to each other. (In addition, we have, of course, electronic vibrations, which, for the present, we shall not consider.) With each one of these types of motion we should expect to find a quantity of energy depending on the number of degrees of freedom of each type. The total energy W_M of a gram-molecule at temperature T should, therefore, be

$$W_M = W_t + W_r + W_V \tag{41}$$

where W_t, W_r, and W_V stand, respectively, for the energy per gram-molecule associated with *t*ranslation, *r*otation, and *v*ibration.

As regards translation, there should be 3 degrees of freedom per molecule, whether the molecule be monatomic or polyatomic. Assuming $\frac{1}{2}k_0T$ of kinetic energy per degree of freedom, we should have

$$W_t = N_0 \cdot 3 \cdot \tfrac{1}{2}k_0T = \tfrac{3}{2}RT \tag{42}$$

As regards rotation, we might expect to find, for a monatomic molecule, 3 degrees of freedom, since such a molecule should be capable of rotation about each of three mutually perpendicular coordinate axes. This should add, per molecule, $W_r = \frac{3}{2}RT$ of kinetic energy. Since the single atom of a *monatomic* molecule of a gas can have no vibration with respect to any other molecule W_V should be zero and, therefore, W_M, *for a monatomic molecule*, should be

$$W_M = W_t + W_r = \tfrac{3}{2}RT + \tfrac{3}{2}RT = 3RT$$

and, for the specific heat at constant volume, we should have

$$C_v = 3R = 5.96 \text{ calories per mole}$$

The values of C_v for the monatomic gases He and Ar at 15°C. are,[1] however,

$$\text{He} \cdots C_v = 2.96 \text{ calories per mole}$$
$$\text{Ar} \cdots C_v = 2.90 \text{ calories per mole}$$

These values are seen to be almost exactly half the value predicted above. Since we know that the molecules of a gas have *translation*, it is usually assumed that, for some reason, the *rotation* of the molecule, *if rotation exists*, does not contribute to the energy of the molecule and, therefore, that the total kinetic energy is that due *to translation only*. For a monatomic molecule, therefore,

$$W_M = W_t = \tfrac{3}{2}RT = 2.98 \cdot T \tag{43}$$

from which $C_v = 2.98$, in agreement with experiment.

We shall discuss, later, the apparent reasons for the "suppression" of these rotational degrees of freedom. For the present, suffice it to remark that this absence, at ordinary temperatures, of the rotational energy of the molecule is in harmony with Rutherford's nuclear type of atom, according to which almost the entire mass of the atom resides in the nucleus, or central "sun," the dimensions of which are very small compared to the dimensions of an atom. The moment of inertia of the atom about any axis through its center of mass must, then, be due, in very large part, to the moment of inertia of the electrons. For argon, for example, which has 18 electrons at a mean distance from the nucleus of the order of, roughly, 10^{-8} cm., the moment of inertia I would be ($I = \Sigma mr^2$) of the order of 10^{-42}, the mass of the electron being 9×10^{-28} grams. The energy of a degree of freedom at 300°K. is ($\bar{E} = \frac{1}{2}k_0T$), about 2.5×10^{-14} ergs. For an argon atom to possess this kinetic energy due to *rotation* would require that its speed of rotation should be of the order of 10^{13} revolutions per second. This is well toward the frequency of visible light. According to the classical theory, then, argon at 300°K. should emit radiation, due to the rotation of the atom, of frequency 10^{13}, which is in the comparatively near infra-red just beyond the visible spectrum. No such radiation from argon is observed. The absence of this radiation *does not explain why* the argon atom does not rotate. It only *confirms* the specific heat observation.

[1] International Critical Tables.

For a diamomic molecule, we have, for translation, $W_t = \frac{3}{2}N_0k_0T$ per gram-molecule. Assuming the molecule to be dumb-bell shaped, *rotation* about the line *joining the two nuclei* should contribute no energy, for the same reason as in a monatomic molecule. Rotation about each of two axes passing through the center of gravity of the dumb-bell and at right angles to each other and to the axis of the molecule involves, however, a much larger moment of inertia. Thus, for O_2, atomic mass 26×10^{-24} grams, distance between atoms of the order of 10^{-8} cm., the moment of inertia is of the order of 10^{-39}. The frequency of rotation required for a kinetic energy equal to that of a degree of freedom at 300°K. is of the order of 10^{12} revolutions per second, which, for radiation, corresponds to a wave length of 0.1 mm. We shall see, from later considerations based on the quantum theory, that this frequency of revolution is permissible. A diatomic molecule may, therefore, have 2 degrees of freedom as regards rotation.

As regards vibration, a diatomic molecule should have 1 degree of freedom. With the kinetic energy $\frac{1}{2}k_0T$, due to vibration, is associated an equal amount of potential energy.

The *total* energy W_M of a gram-molecule of a diatomic gas should be given by

$$W_M = \tfrac{3}{2}RT + \tfrac{2}{2}RT + \tfrac{2}{2}RT = \tfrac{7}{2}RT$$

Therefore, C_v should be $\frac{7}{2}R$, or 6.95 calories per mole per degree. The following data, however, give the molecular heat of four common, diatomic gases at 15°C.:

GAS	CALORIES PER MOLE PER DEGREE
H_2	4.92
N_2	4.94
O_2	4.94
CO	5.02

These observed values are very nearly $\frac{5}{2}R$ ($\frac{5}{2}R = 4.97$) instead of $\frac{7}{2}R$. From this, we may conclude that *one* of these predicted groups of degrees of freedom is absent. According to the quantum theory, the energy per degree of freedom at 300°K. is not sufficient to "activate" the vibratory degrees of freedom. W_v is, therefore, for ordinary temperatures, zero. We have, accordingly, for a diatomic molecule,

$$W_M = W_t + W_r = \tfrac{3}{2}RT + \tfrac{2}{2}RT = \tfrac{5}{2}RT \qquad (44)$$

and for the molecular heat C_v,

$$C_v = 5/2 R$$

For a triatomic molecule, such as H_2O, CO_2, or SO_2, we should have 3 degrees of freedom in respect of translation; 3 in respect of rotation, if we assume that the nuclei do not make a linear molecule (*i.e.*, all three in a straight line); and none for vibration, assuming the "vibratory" degrees of freedom to be suppressed, as in the case of a diatomic molecule. We should, therefore, have, for a triatomic molecule,

$$C_v = 3/2 R + 3/2 R = 3R = 5.96 \text{ calories per mole per degree} \quad (45)$$

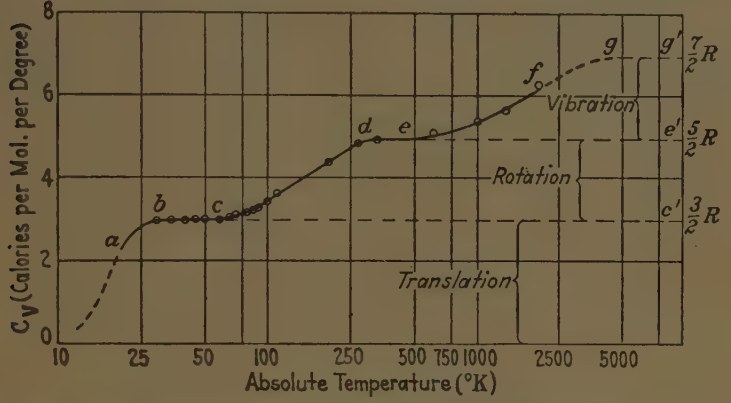

FIG. 69.—Showing the variation with temperature of the contribution to molecular heat of energy due to translation, rotation, and vibration.

Actually, the molecular heat of water vapor at 50°C. is 5.96 calories per mole per degree. That for CO_2 at 20°C. is about 6.2. These values are in reasonable agreement with theory.

This agreement between classical theory and experiment is, however, to be regarded as fortuitous. We find quite another story when we come to consider the variation of the specific heat of gases with temperature.

(*b*) *Variation of the Molecular Heat of Gases with Temperature.*—This variation is best illustrated by data on hydrogen, which, because of its peculiar importance, has been extensively studied. The data, compiled from several sources,[1] are given in Table X and are shown graphically in Fig. 69, in which temperature is plotted to a logarithmic scale. In this curve, the observed data

[1] LEWIS: "Quantum Theory;" KEMBLE and VAN VLECK, *Phys. Rev.*, vol. 21, p. 653 (1923).

are shown by the small circles. The data in the square brackets at the beginning of the table are not plotted, since, except for the temperature 29.6°K., they were not corrected[1] to constant volume. These data for the three temperatures 18.6, 21.2, and 24.0°K., are, therefore, represented qualitatively by the full line *ab* of the graph.

TABLE X.—VARIATION OF THE MOLECULAR HEAT OF HYDROGEN WITH TEMPERATURE

T, degrees Kelvin	C_v, calories per mole per degree	T, degrees Kelvin	C_v, calories per mole per degree
18.6	[2.70	85	3.21
21.2	2.78	90	3.26
24.0	3.02	100	3.42
29.6	3.20 ≡ 2.98]	110	3.62
35	2.98	196	4.39
40	2.98	273	4.84
50	3.01	333	4.91
60	2.99	625	5.08
65	3.04	1,000	5.34
70	3.10	1,399	5.62
80	3.14	2,000	6.34

Figure 69 is very instructive. The experimental values show an increase in C_v from point a, corresponding to some 2 calories per mole per degree at 20°K. to over 6 calories per mole per degree at 2000°K. (The dotted lines at either end of the graph are hypothetical, and qualitative, extensions.) Taking the graph as a whole, the increase from a to f is seen to take place in three steps:

1. From the lowest temperatures, C_v rises rapidly to a maximum at point b corresponding to 2.98 ($=\frac{3}{2}R$) calories per mole per degree at about 30°K. From b to c, 30 to 60°K., C_v remains constant at $\frac{3}{2}R$, and in this region H_2 behaves as a *monatomic* gas. Now, $\frac{3}{2}R$ is the energy W_t, which we associate with *translation*. The graph *abcc'*, therefore, represents the variation, with temperature, of C_v, due to the "translatory" degrees of freedom of the molecule. *Were there no other kinds of degrees of*

[1] LEWIS: "Quantum Theory," p. 106.

freedom, the value of C_v would remain constant with temperature above 60°K., as is indicated by the dotted line *cc'*.

2. At point *c*, corresponding to about 60°K., a second increase begins. C_v rises until point *d* is reached, corresponding to 4.97 calories per mole per degree ($= \frac{5}{2}R$) at a temperature in the neighborhood of 350°K. For a short range *d* to *e*, C_v remains constant at this value, which is the value predicted by classical theory (equation (44)) after deleting the vibratory degrees of freedom and the rotation about the molecular axis. We may, therefore, conclude that this second rise *c* to *d* is due to the *gradual* bringing into play of the two "rotational" degrees of freedom. The curve *cdee'*, therefore, represents the variation, with temperature, of that part of the specific heat which is due to molecular rotations. We thus see that below 60°K. either the hydrogen molecule has no rotational energy or, rather, that such rotational energy, *if rotation exists*, does not vary with temperature.
3. Beginning at point *e*, a third rise in molecular heat is observed. Data in the region *e* to *f* (500 to 2000°K.) can hardly be regarded as more than qualitative, but there is little doubt that an actual increase in C_v does take place above 500°K. We may ascribe this increase to the activation of the "vibratory" degrees of freedom. The part of the curve *efgg'*, largely qualitative, represents the variation, with temperature, of that part of C_v which is due to vibratory motion of the two atoms of the hydrogen molecule with respect to each other.

Each of these three increases in C_v with increasing temperature, namely, *a* to *b*, *c* to *d*, and *e* to *g*, are suggestive of the increase with temperature in the atomic heat of solids, as shown in the curves in Fig. 66. We have seen that an approximate solution of the problem of the variation of the specific heat of solids with temperature was made by introducing the quantum postulate, that the energy per degree of freedom is given by

$$\frac{h\nu}{e^{h\nu/k_0T} - 1}$$

Einstein and Stern[1] applied this same principle to the *rotation* of the molecules and computed the variation of rotational specific

[1] *Ann. Physik*, vol. 40, p. 551 (1913).

heat with temperature. Here, ν is taken as the (constant) frequency of rotation of the molecule. Of course, this frequency *must* vary with the rotational energy of the molecule. Further attempts to explain the variation of rotational specific heats with temperature have been made by Ehrenfest, Kemble, Van Vleck, and others.[1] The reader is referred to the original articles.

Bjerrum[2] has applied Einstein's theory of specific heats to the atomic vibrations of polyatomic molecules of a gas in order to compute specific heats at high temperatures—the region represented by e to g, in Fig. 69. For CO_2, for example, in the equation

$$C_v = C_t + C_r + C_V$$

where C_t, C_r, C_V are the respective contributions to C_v, due to *t*ranslation, *r*otation, and *v*ibration, Bjerrum assumes

$$C_t = \tfrac{3}{2}R$$
$$C_r = \tfrac{3}{2}R$$

in accordance with the discussion above. (The temperature is supposed to exceed that corresponding to point d of Fig. 69; and, since the molecule CO_2 is *tri*atomic, all three of the *rotational* degrees of freedom are active.) For C_V, Bjerrum uses a formula of the Nernst-Lindemann type for the specific heat of solids, in which two infra-red frequencies are inserted: $\nu_1 = 0.60 \times 10^{14}$, and $\nu_2 = 0.37 \times 10^{14}$. Reasonably good agreement with experiment is obtained. Carbon dioxide is known to possess three absorption bands in the infra-red, as follows:

$$\nu_1' = 0.204 \times 10^{14} \text{ sec.}^{-1}$$
$$\nu_2' = 0.70$$
$$\nu_3' = 1.1$$

If these *three observed* values of frequency for CO_2 be used instead of ν_1 and ν_2, the agreement with experiment is found to be almost as good.[3]

[1] P. EHRENFEST: *Verh. d. deusch. Phys. Ges.*, vol. 15, p. 451 (1913); KRÜGER: *Ann. Physik*, vol. 50, p. 396; vol. 51, p. 450 (1916); REICHE: *Ann. Physik.*, vol. 58, p. 657 (1919); MACDOUGAL: *Journ. Amer. Chem. Soc.*, vol. 43, p. 23 (1921): KEMBLE and VAN VLECK: *Phys. Rev.*, vol. 21, p. 653 (1923). See also a summary by REICHE, "The Quantum Theory" (English translation, Chap. V).

[2] LEWIS: "Quantum Theory," 3d ed., Chap. IV.

[3] LEWIS: "Quantum Theory," p. 84.

These infra-red frequencies of polyatomic molecules due to molecular rotations and vibrations play a very important part in the general scheme of spectra.[1]

We can see, in a general way, how the expression

$$\frac{h\nu}{e^{h\nu/k_0T} - 1}$$

can be applied to the *rotations* or to the *vibrations* of polyatomic molecules in order to explain the corresponding variations of specific heat with temperature. Two of the three parts of the curve in Fig. 69 are, thus, qualitatively accounted for. But the third part of the curve, *a* to *b*, exhibits a like variation with temperature. Do we have here, also, the same type of explanation of the rise of C_v with temperature? It is difficult to see how we can apply to the *translatory* motion of gas molecules any formula involving a *frequency*, since, for such motion, *frequency* can have, *ordinarily*, no meaning. Various attempts have been made to apply the quantum theory to translations. Thus, Nernst postulates that at *very* low temperatures the translatory motion of the molecules "degenerates" into a kind of circular motion (revolution around some fixed point *not* within the molecule) and that the energy $\overline{U}$ of a molecule in this *degenerate* state is given by

$$\overline{U} = \frac{3}{2} k_0 T \frac{h\nu}{e^{h\nu/k_0T} - 1}$$

where ν may now have a *physical* meaning: namely, the *frequency* of revolution of the molecule in its orbit. This "picture" is exceedingly artificial. The variation of the "translatory" specific heat of gases with temperature can hardly be said to have received even a *qualitatively* satisfactory explanation.[2] One might, perhaps, apply Compton's method (see p. 275) of the "agglomeration" of degrees of freedom by assuming that when the relative energy with which 2 molecules collide falls below a certain minimum value ϵ, the molecules coalesce, with a consequent reduction in the number of degrees of freedom and, therefore, of C_v.

11. The Suppression of Degrees of Freedom.—The quantum theory, *granted its premises*, offers a ready "explanation" of the suppression (to which attention was called in the preceding

[1] "Molecular Spectra in Gases," *Nat. Research Council, Bull.* 57 (1926).

[2] See LINDEMANN: *Phil. Mag.*, vol. 39, p. 21 (1920).

section) at sufficiently low temperatures, of the rotational and the vibrational degrees of freedom. According to the quantum theory, a vibratory (atomic or electronic) mechanism or oscillator of frequency ν may have 0, 1, 2, 3 . . . quanta of energy $h\nu$. If we know, or can compute, the frequency ν of an oscillator, we may, at once, calculate the *least* amount of energy, *i.e.*, 1 quantum, which the oscillator may have, if it possesses any energy at all. If the temperature T of the system with which the oscillator is associated is such that $h\nu$ is considerably in excess of the *average* energy per degree of freedom of the system $\frac{1}{2}k_0T$, *i.e.*, if

$$h\nu >> \tfrac{1}{2}k_0T \tag{45}$$

only very rarely will it happen, according to Maxwell's distribution law, that the oscillator, as a result of the statistical exchanges of energy in the system, will be given a "chance" to acquire as much energy as $h\nu$. Or, in other words, of a large number of such oscillators, only very rarely will one be found with any energy. The relative values, therefore, of $h\nu$ and k_0T determine the "activity" of any type of degree of freedom.

(*a*) *Rotation.*—We shall see, later (Chap. X), that the quantum conditions applied to a rotating system, such as a molecule (monatomic or polyatomic), require that the angular momentum M_θ of the system be restricted to integer multiples of $h/2\pi$, h being Planck's constant, *i.e.*,

$$M_{\theta,\tau} = \tau \cdot \frac{h}{2\pi} \tag{46}$$

where τ may be any integer—0, 1, 2, 3 . . .—and $M_{\theta,\tau}$ is the angular momentum corresponding to a particular value of τ. Since

$$\left.\begin{aligned} M_\theta &= I \cdot 2\pi\nu \\ \text{and} \qquad E_k &= \tfrac{1}{2} \cdot I \cdot (2\pi\nu)^2 \end{aligned}\right\} \tag{47}$$

where I is the moment of inertia, ν is the frequency of rotation, and E_k is the kinetic energy, we have, by combination of equations (46) and (47),

$$E_{k,\tau} = \tau^2 \frac{h^2}{8\pi^2 I} \tag{48}$$

$E_{k,\tau}$ is the kinetic energy for the particular value of τ. If we know the moment of inertia I of the rotating system, we can

compute, at once, the series of values of kinetic energy which, under the quantum rules, the system may possess.

For a monatomic molecule, such as argon, we saw (p. 279) that the moment of inertia was of the order of 10^{-42} gm.-cm.^{2} The smallest possible quantity, therefore (other than zero), of kinetic energy of rotation which the argon atom could possess is found by putting $\tau = 1$ and $I = 10^{-42}$ in the equation (48). This gives

$$E_{k,1} = 1^2 \frac{(6.5 \times 10^{-27})^2}{8\pi^2 \cdot 10^{-42}} = 5.5 \times 10^{-13} \text{ ergs}$$

The average energy per degree of freedom at 300°K. is about 2.5×10^{-14} ergs (*i.e.*, $\frac{1}{2} \times 1.37 \cdot 10^{-16} \times 300$). We see, therefore, that the smallest rotational energy which an argon atom may possess is some twenty times the average energy per degree of freedom at 300°K. Clearly, then, the rotational degrees of freedom of argon are not active at 300°C. The atomic heat should be due solely to translation. This, as mentioned above, is found to be the case.

On the other hand, for a diatomic molecule, such as H_2, rotating about an axis perpendicular to and bisecting the line joining the two atoms, we have a much larger moment of inertia. Taking the mass of a hydrogen atom as 1.6×10^{-24} grams and the distance between the 2 atoms of the H_2 molecule as of the order of 10^{-8} cm., the moment of inertia I_{H_2} of the molecule is

$$I_{H_2} = \tfrac{1}{2} \times 2 \cdot 1.6 \cdot 10^{-24} \times (10^{-8})^2 = 3 \times 10^{-40} \text{ gram-cm.}^2$$

Inserting this value in equation (48) gives, for $\tau = 1$, about 0.2×10^{-14} erg as the minimum rotational energy permissible on the quantum hypothesis. We see that this is much *smaller* than the average energy per degree of freedom at 300°K. Consequently, the 2 rotational degrees of freedom of H_2 should be active at 300°K. (The third, namely, that about the axis joining the 2 atoms, should be inactive, as in the case of the monatomic molecule, since the moment of inertia of the H_2 molecule about this axis is of the order of 10^{-44}.) The molecular heat of H_2 at 300°K. should, therefore, be $\frac{5}{2}R$, which is the experimental value.

(*b*) *Vibration.*—We know, from the phenomena of band spectra (see Chap. X, Sec. 15), that the frequency of vibration, with respect to each other, of the atoms of a polyatomic molecule of a gas corresponds to infra-red frequencies of the order of 10^{14} sec.$^{-1}$. A quantum of this frequency is of the order of 10^{-13} ergs. This is

considerably *more* than the average energy per degree of freedom at 300°K. We should, therefore, not expect the vibrational degrees of freedom to be active at that temperature.

The computations in this section are, of course, only roughly quantitative. They should be taken as illustrative rather than as of numerical significance.

CHAPTER IX

SERIES RELATIONS IN LINE SPECTRA

We saw, in Chap. VII, that attempts to explain the experimentally observed laws of the distribution of energy in the continuous spectrum emitted by a black body were unsuccessful until Planck introduced the revolutionary concept of radiation quanta. Planck's hypothesis became both *possible and necessary*, because the very careful experiments of Lummer and Pringsheim had proved that Wien's law of temperature radiation was untenable.

A somewhat similar sequence of events is to be found in the development of our present rapidly growing knowledge of the characteristic *line* spectra of atoms and molecules. Corresponding to the empirical laws of temperature radiation, there was accumulated in the field of line spectra a vast array of very accurate measurements of the wave lengths of lines in the spectra of various substances, considerable impetus being given to this work because of the rigorous demands of spectroscopy as a method of chemical analysis. From these data, certain relations were empirically discovered between the frequencies of various lines in the spectra of certain of the elements. Spectral lines the frequencies of which are related to each other in a regular sequence are said to form a *series*. Similarities among such series in the spectra of the several elements or substances pointed to some fundamental mechanism, common to all atoms, as the origin of characteristic line spectra. The gradual accumulation of evidence bearing on the problem of atomic structure, on the one hand, and the increasing importance of these spectral series relationships, on the other, culminated, about 1913, in the proposal, by Bohr, of the now famous theory of atomic structure and the origin of spectra which bears his name. The concept of radiation quanta, introduced by Planck to explain the laws of the *distribution of energy* in *temperature* radiation, played a very fundamental role in Bohr's theory of the laws of the *distribution of frequencies* in *characteristic* radiation.

In this chapter, we shall consider, briefly, the development of the empirical laws of spectral series. One can fully appreciate our present knowledge of this subject and its bearing on the problems of atomic structure and the nature of radiant energy only by understanding how, out of an apparently almost hopeless mass of tangled numerical data, these spectral-series relationships were sifted. No subject illustrates better the patient, persistent effort necessary to the advancement of scientific knowledge.

1. Units and Methods of Measurement. (*a*) *Wave Lengths.* In spectral measurements we are concerned, sometimes with the wave lengths of lines; sometimes with frequencies. The meter, or the centimeter, is the basis of practically all wave-length measurements. To express the wave length of a line in, or near, the visible region of the spectrum in meters is, however, awkward because of the very small decimal required. Various submultiples of the meter are, therefore, employed as units of length in different parts of the spectrum, *viz.*,

The micron,[1] symbol μ $= 10^{-4}$ cm. (or 10^{-6} meters)
The millimicron, symbol $m\mu$ $= 10^{-7}$ cm.
The Ångström, symbol Å $= 10^{-8}$ cm.
The X-unit, symbol X.U. $= 10^{-11}$ cm.

The last named is used in the X-ray region of the spectrum.

To illustrate these several units, the wave length of the red cadmium line may be expressed, variously, as

0.000064384696 cm.
0.64384696 μ (microns)
643.84696 $m\mu$ (millimicrons)
6438.4696Å (Ångströms)[2]

[1] The prefix "micro" connotes "millionth;" the prefix "milli" connotes "thousandth," as in "milliampere" or "microampere."

[2] Strictly speaking, the Ångström is not defined from the meter as a *primary* standard of length. Michelson and Benoist in 1895 and, later (1907), Fabry, Perot, and Benoist measured the wave length of the red cadmium line in terms of the standard meter. The two measurements were almost exactly in agreement, the wave length according to the latter measurement being

6438.4696 Ångströms

The International Union for Solar Research, in 1907, adopted this value of the wave length of the red cadmium line as the *primary* standard of wave

(*b*) *Frequency and Wave Number.*—Wave lengths of lines are of fundamental importance in the technique of spectroscopy and in spectroscopic analysis. In physical theory, on the contrary, *frequency* ν is more fundamental than wave length. We do not, however, measure frequencies *directly*. Laboratory measurements yield *wave lengths*. Frequencies are *computed* from these measured values of wave length λ and from the velocity of light c by the relation

$$c = \nu \cdot \lambda$$

Frequencies may be expressed in vibrations per second. This involves very large numbers, of the order of 10^{14} for the visible region. For many purposes, it is more convenient to use, as proportional to frequency, the *number* of waves per centimeter, symbol n. Thus,

$$n = 1/\lambda \text{ cm.}^{-1}$$

where λ is expressed in centimeters. Thus, the *wave number* n of the red cadmium line is 15,526.84 cm.$^{-1}$. Both wave number and wave length vary with the medium in which the radiation is propagated. Corrections to standard conditions, usually to vacuum, are made. When so corrected, wave numbers are *strictly* proportional to frequency. Frequency, in vibrations per second, is, of course, dependent only on the source and not on the medium through which the radiation is propagated.

(*c*) *Methods.*—It is quite beyond the scope of this book to discuss the technique of spectroscopic measurements. The student is referred to the many excellent treatises on the subject.[1] Direct measurements of wave lengths of light are based on the phenomenon of interference. Thomas Young, in 1801, was the first to make such estimates of wave lengths (see Chap. III) from data given by Newton on Newton's rings. Twenty years later, Fraunhofer developed the diffraction grating as a method of measuring wave lengths. At first, he used equally spaced wires wound on a frame. Later, he ruled lines on a glass—of the order of 8,000 per inch. The next important step in the improvement

length on the basis of which all other wave lengths were to be expressed. Formally, this amounts to a new definition of the Ångström in terms of the wave length of the cadmium line such that this wave length is *exactly* 6438.4696 Ångströms. Other wave lengths are expressed in terms of the Ångström so defined.

[1] BALY, E. C. C.: "Spectroscopy;" HICKS, W. M.: "The Analysis of Spectra;" FOWLER, A.: "Report on Series in Line Spectra."

in the technique of wave-length measurements was made by Ångström, who, in 1868, published an elaborate table of wave lengths of lines in the solar spectrum, made by three carefully ruled gratings. Measurements with gratings, approaching modern accuracy, were made by Rowland, who, about 1885, introduced the concave reflecting grating and greatly improved the technique of ruling gratings and of using them. Michelson's introduction of the interferometer and his use of that instrument, in 1895, for measuring the number of wave lengths of the red cadmium line in the standard meter[1] marks the latest important step in precision measurements of wave lengths. Hicks[2] gives the following values of measurements of the wave length of the D_1 line of sodium as evidence of improvement in spectroscopic measurements:

Fraunhofer (1822).....	5887.7	Ångströms
Ångström (1864–9).....	5895.13	
Rowland (1887–1893).....	5896.156	
Michelson[1] (1887–1893).....	5895.932	

[1] Computed by Fabry and Perot.

Michelson's measurement of the wave length of the cadmium line as 6,438.4696 Ångströms[3] and the subsequent adoption of this as a *primary* standard, were succeeded by the adoption of a group of *secondary* standard lines based on this primary standard and extending at conveniently spaced intervals throughout the spectrum. From these, in turn, a group of more closely spaced *tertiary* standards has been prepared. Measurements of wave lengths in the visible and near-visible region of the spectrum are now possible with an absolute accuracy (in terms of the centimeter) of considerably better than 1 part in a million. The relative accuracy (in terms of the Ångström) is considerably higher.

2. Early Search for Series Relations in Spectra.—As soon as dependable wave-length measurements became available, numerous investigators, reasoning from the analogy of overtones in acoustics, sought for harmonic relations in the lines found in the spectrum of a given element. This search was the more promising, since certain regularities had already been noted. Thus,

[1] For description of the method used by Michelson, see his "Studies in Optics." University of Chicago Press (1927).

[2] "Analysis of Spectra," p. 4.

[3] See note, p. 290.

Mascart, in 1869, pointed out that there were several *pairs* of lines in the spectrum of sodium.

In 1871, Stoney[1] discovered a very suggestive integer relation between certain of the lines of the hydrogen spectrum. If a certain number, 131,277.14, be divided, in turn, by 20, 27, and 32, the quotients gave, respectively, the wave lengths of first (red), second (blue), and fourth (violet) lines of hydrogen. Thus:

Divisor	Quotient	Observed wave length, Ångströms
20	6563.86	6563.96
27	4862.12	4862.11
32	4102.41	4102.37

Further search for such integer relations proved fruitless, and, in 1881, Schuster[2] showed that the number of cases found where such integer relations between lines exist is not greater than might be expected from probability considerations.

The papers of Liveing and Dewar,[3] in the early eighties, emphasized the physical similarities occurring in the spectra of such elements as the alkali metals. They called attention to the successive *pairs* of lines in the spectrum of sodium and pointed out that these pairs were alternately "sharp" and "diffuse" and that they were more closely crowded together toward the short-wave-length end of the spectrum, suggesting some kind of series relation, which, however, they were unable to discover.

A little later, Hartley[4] discovered an important numerical relationship between the components of doublets or triplets in the spectrum of a given element: If frequencies, instead of wave lengths, be used, Hartley found that *the difference in frequency between the components of a multiplet* (*i.e.*, doublet or triplet) *in a particular spectrum is the same for all similar multiplets in that spectrum.* Hartley's law is illustrated by Table I, which shows, in modern measurements, the wave-number differences Δn between the components of a series of triplets in the spectrum of

[1] *Phil. Mag.*, vol. 41, p. 291 (1871).
[2] *Proc. Roy. Soc.*, vol. 31, p. 337 (1881).
[3] *Proc. Roy. Soc.*, vol. 29, p. 398 (1879); vol. 30, p. 93 (1880).
[4] *Jour. Chem. Soc.*, vol. 43, p. 390 (1883).

TABLE I.—COMPONENT DIFFERENCES Δn IN A SERIES OF TRIPLETS IN THE SPECTRUM OF Zn

(Wave lengths λ and wave numbers n, taken from Hicks' "Analysis of Spectra," p. 280)

	λ (Ångströms)	n, centimeter^{-1}	Δn, centimeter^{-1}
1	4,810.54	20,781.2	
			388.9
	4,722.16	21,170.1	
			190.1
	4,680.14	21,360.2	
2	3,072.19	32,540.8	
			388.7
	3,035.93	32,929.5	
			190.1
	3,018.50	33,119.6	
3	2,712.60	36,854.3	
			388.7
	2,684.29	37,243.0	
			189.9
	2,670.67	37,432.9	
4	2,567.99	38,929.6	
			389.7
	2,542.53	39,319.3	
			189.4
	2,530.34	39,508.7	
5	2,493.67	40,089.6	
			388.9
	2,469.72	40,478.5	
			187.5
	2,457.72	40,676.0	

zinc. The difference in wave numbers between the first and second component of the series of triplets is very close to 389; between the second and third, 189.[1] The agreement among these

[1] Wave lengths are usually given for air at a standard pressure and temperature. Values of wave numbers, however, are expressed as the reciprocal of the wave length reduced to vacuum. These reductions are made by means of empirical formulæ or by tables based on those formulæ (see Hicks, *loc. cit.*). This accounts for the fact that the values of n in the above table are not quite equal to the reciprocal of λ.

differences is so striking as to point, almost with certainty, to some fundamental underlying law governing the emission of these lines by the zinc atom. The early workers were, thus, apparently justified in the belief that numerical relations among the multiplets themselves awaited discovery.

Hartley's law made it possible to isolate from the large number of lines in any given spectrum those groups of lines which were undoubtedly related. But the task was not an easy one. Figure 70 shows the lines in the zinc spectrum from about 2500 to 2800 Ångströms which region includes the third and the fourth triplets shown in Table I. It is by no means obvious which of these many lines are associated by Hartley's law. The two triplets given in Table I are marked by crosses (×) in Fig. 70. This same spectral region, however, contains another overlapping series of triplets, which are designated by circles (○). Clearly,

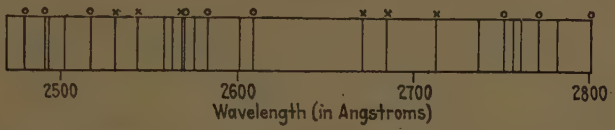

FIG. 70.—Some lines in the spectrum of zinc in a limited wave-length range in the ultra-violet. The lines marked with a cross (×) are the triplets shown in Table I. The lines marked (○) belong to another series of triplets.

the sorting out of these related lines required a great deal of diligent and patient study.

3. Balmer's Formula for the Hydrogen Spectrum.—The real beginning of our knowledge of spectral-series formulæ dates from the discovery by Balmer,[1] in 1885, that the wave lengths of the nine then known lines in the spectrum of hydrogen could be expressed by the very simple formula

$$\lambda = h\frac{m^2}{m^2 - 4} \qquad (1)$$

where h is a constant the numerical value[2] of which, to give λ in Ångströms, is 3645.6 and m is a variable integer which takes on the successive values 3, 4, 5 . . . for, respectively, the first (beginning at the red) second, third . . . line in the spectrum.

Balmer discovered first, apparently in the course of his search for integer relations between the wave lengths of lines, that the

[1] *Ann. Physik*, vol. 25, p. 80 (1885).

[2] Balmer used also the value 3645.0 as an approximate mean.

wave lengths (in Ångströms) of the four hydrogen lines in the visible spectrum, which lines had been very carefully measured by Ångström, were given, within experimental error, by multiplying the number 3645.6 by $\frac{9}{5}$, $\frac{4}{3}$, $\frac{25}{21}$, and $\frac{9}{8}$. He observed that these four fractions made no regular series. If, however, the numerator and denominator of the second and of the fourth be multiplied by four the series becomes $\frac{9}{5}$, $\frac{16}{12}$, $\frac{25}{21}$, $\frac{36}{32}$. The numerators of these fractions make the series 3^2, 4^2, 5^2, 6^2 . . . ; while the denominators are these same squares decreased by four. The series is thus given by putting into the fraction

$$\frac{m^2}{m^2 - a^2}$$

the value 2 for a, and the successive values 3, 4, 5 . . . for m.

Balmer compared the predictions of this formula (equation (1)) with the best available values then known for the wave lengths of the hydrogen lines. The four lines in the visible region had been measured by Ångström, Mendenhall, Mascart, and Ditscheiner. Five ultra-violet lines in the spectrum of white stars had been measured by Huggins. Table II, taken from Balmer's paper, shows the comparison of the formula with the measurements of Ångström and of Huggins. The agreement is seen to be excellent

TABLE II.—WAVE LENGTHS OF THE FIRST NINE HYDROGEN LINES COMPUTED BY BALMER FROM HIS FORMULA $\lambda = 3645.6\frac{m^2}{m^2 - a^2}(a = 2)$

Line	m	λ (computed), Ångströms	λ (observed) Ångströms
H_α	3	6562.08	6562.10 (Ångström)
H_β	4	4860.80	4860.74 (Ångström)
H_γ	5	4340.0	4340.10 (Ångström)
H_δ	6	4101.3	4101.2 (Ångström)
H_ϵ	7	3969.7	3968.1 (Huggins)
H_ξ	8	3888.6	3887.5 (Huggins)
H_η	9	3835.0	3834.0 (Huggins)
H_ϑ	10	3797.5	3795.0 (Huggins)
H_ι	11	3770.2	3767.5 (Huggins)

in the visible spectrum. The discrepancy between Balmer's computed values and the measurements of Huggins increases to nearly 1 part in 1,000 for H_ι. Balmer questioned whether this discrepancy indicated that the formula was only an approxima-

tion or whether the data were in error. Recent measurements have considerably revised Huggins' data but have also revealed the need for a slight correction to Balmer's formula. We shall return to this point later.

Balmer correctly predicted that in this series of lines in hydrogen no lines of longer wave length than H_α would be found and that the series should "converge" at $\lambda = 3645.6$ Ångströms, since the fraction $\frac{m^2}{m^2 - a^2}$ approaches unity as m becomes larger.

The impetus which Balmer's discovery gave to work in spectral series is another illustration of the highly convincing nature of relations which are expressible in *quantitative* form. Soon after the publication of Balmer's work, intensive investigations in spectral series were initiated by Kayser and Runge and by Rydberg. We shall discuss Rydberg's work because of its important bearing on subsequent developments.

4. Rydberg's Formula for Spectral Series. (*a*) *Some Types of Series.*—Balmer, in the article announcing his discovery, raised the question whether his formula might not be a special case of a more general formula applicable to other series of lines in other elements. Rydberg[1] succeeded in finding this more general formula. Using the comparatively large mass of wave-length data then available and starting from the above-mentioned work of Liveing and Dewar, Rydberg isolated still other series of doublets and triplets of constant frequency difference, according to Hartley's law of constant wave-number separation. He then had at hand a reasonably large number of series of lines from different elements. The lines in any given series tended to crowd together toward the ultra-violet, and Rydberg found that this spacing followed some kind of regular law. For, if either the wave lengths or the wave numbers of the lines in a given series (the lines belonging to the series, be it recalled, being identified by Hartley's law of constant frequency difference in doublets or triplets) were plotted as ordinates against the number of the line in the series as abscissæ, smooth curves resulted. Thus, in the spectrum of sodium are found numerous doublets of which the well-known yellow *D* lines are the most intense. Table III[2] shows the first

[1] A brief, thought not very satisfactory, account of Rydberg's work is given by him in *Phil. Mag.*, vol. 29, p. 331 (1890). A fuller account is given in Baly's "Spectroscopy."

[2] Taken from FOWLER'S "Report on Series in Line Spectra."

TABLE III.—DOUBLETS IN THE SPECTRUM OF SODIUM

Wave length, Ångströms	Wave number, cm.$^{-1}$	Ordinal number	Ordinal number omitting $\lambda = 5{,}889.9$	Series number	
				Sharp	Diffuse
11,404.2	8,766	1	1	1	
8,194.8	12,199	2	2		1
6,160.7	16,227	3	3	2	
5,889.9	16,973	4			
5,688.2	17,575	5	4		2
5,153.6	19,398	6	5	3	
4,982.9	20,063	7	6		3
4,751.9	21,038	8	7	4	
4,668.6	21,414	9	8		4
4,545.2	21,995	10	9	5	
4,497.7	22,227	11	10		5
4,423.3	22,601	12	11	6	
4,393.4	22,755	13	12		6
4,344.8	23,010	14	13	7	

14 of these doublets, only the component of shorter wave length being given. (The wave lengths of the two *D* lines are 5,889.963 and 5,895.930 Ångströms, respectively.) The spacing of these lines on a wave-number scale is shown in the strip *AB* at the left edge of Fig. 71. The spacing between the lines decreases toward higher wave numbers (shorter wave lengths) but the spacing is not regular. If the wave numbers of these lines be plotted as ordinates against the ordinal number of the line (the numbers shown in the third column of Table III) as abscissæ, the graph *abcd* (Fig. 71) results, with a break at *bc*, the point represented by the double circle being the *D* line. From *c* to *d* it is seen that alternate points fall on a smooth curve, the other points being below the curve. If, however, we discard from the series the line $\lambda = 5{,}889.9$ Ångströms and plot wave numbers against the ordinal numbers given in the fourth column, the smooth curve *abef* through the solid circles results, *the alternate points shown by the hollow circles falling regularly below the curve.* We evidently have here two nearly parallel *series* of lines (really, four series, since each of the plotted points represents a doublet)—one series shown by the solid circles; the other by the hollow circles. The two series, as thus isolated, have the distinguishing *physical* characteristics that the former consists of *sharp* lines and is,

therefore, called the *sharp* series; the latter, of *diffuse* lines and is called the *diffuse* series. The ordinal numbers of the lines in each of these two series are shown in columns five and six of table III. (The discarded line $\lambda = 5{,}889.9$ belongs to still another series, the *principal* series, the remaining lines of which are in the ultra-violet, the second line of this series being at $\lambda = 3{,}302.34$.)

(*b*) *Graphical Relations.*—That these two series are similar, so far as concerns the relation of the frequencies of the several lines

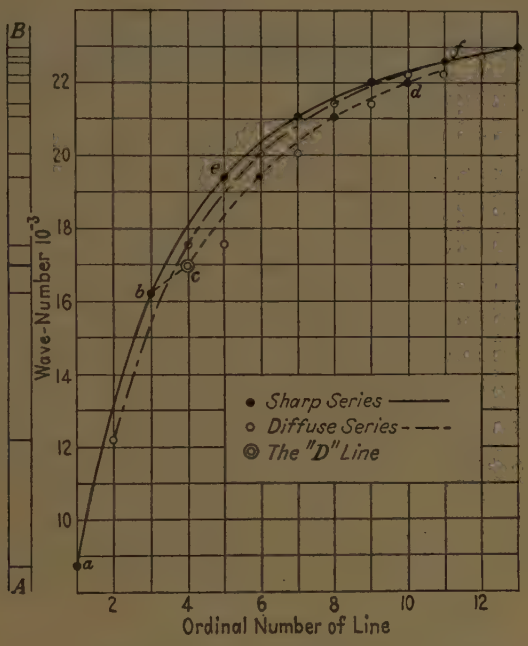

FIG. 71.—The sharp and the diffuse series of sodium.

to their respective ordinal numbers, is qualitatively evident from Fig. 71. Rydberg observed, in this way, that such a similarity existed not only among the several series of a given element but also among series of different elements. He then showed that this similarity was *quantitative*. His method is illustrated by Table IV and Fig. 72. The *difference* in wave numbers between successive lines in the two series in the sodium spectrum given in Table III are computed and recorded in columns two and three of Table IV.

TABLE IV.—WAVE-NUMBER DIFFERENCE Δn BETWEEN SUCCESSIVE LINES IN THE SHARP AND THE DIFFUSE SERIES OF SODIUM

Difference	Δn, in wave numbers		Ordinal number of difference
	Sharp	Diffuse	
1 to 2	7461	5376	1
2 to 3	3171	2488	2
3 to 4	1640	1351	3
4 to 5	957	813	4
5 to 6	606	528	5
6 to 7	409	.....	6

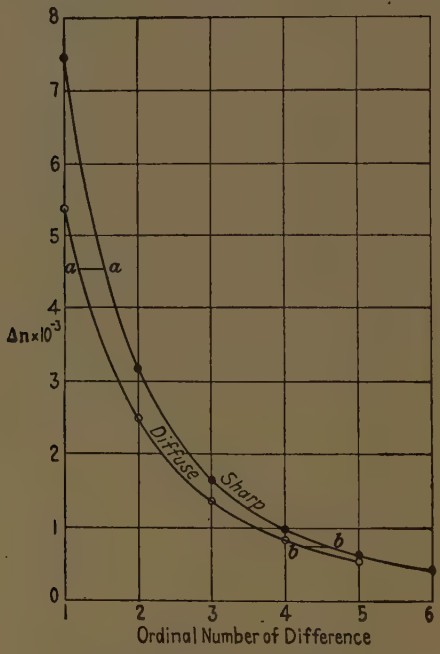

FIG. 72.—Wave-number differences between successive lines in the sharp and the diffuse series of sodium.

These *differences* are then plotted as ordinates against the *ordinal number* of the *difference* (column four) as abscissæ, giving the two curves shown in Fig. 72. These curves are *exactly* parallel, the horizontal lines *aa* and *bb* being *exactly* equal. The two curves would, thus, coincide, if the one for the diffuse series were displaced horizontally toward the right by a distance μ equal to

the length of the line *aa*. In short, the values Δn_s of the successive differences for the *sharp* series are the same function f of $(m + \mu)$ as the corresponding differences Δn_d for the diffuse series are of m, where m is the ordinal number of the difference. (Note that μ is less then 1 ordinal unit.)

Rydberg found: (1) that frequency-difference curves plotted in this way for a large number of series for various elements were parallel to each other; and (2) that, by a proper choice of the ordinal number of the differences, it was always possible to make *less than unity* the value of the horizontal displacement μ required to shift any curve into coincidence with one chosen as a standard. By giving μ a suitable value, therefore, for each series, the curves were identical in form, a fact which can be expressed by the equation

$$\Delta n_i = f(m + \mu_i) \tag{2}$$

when f is some function, to be determined, of $(m + \mu_i)$; μ_i is the "shift," characteristic of a particular series i the wave-number differences of which are Δn_i; and m is the ordinal number so chosen as to make μ_i less than unity.

(*c*) *A General Formula.*—Equation (2), since it contains Δn, is somewhat analogous to a differential equation. We are, however, more interested in *wave numbers* n than in wave-number *differences* Δn. By a procedure, partially empirical, we can determine a relation between n and $(m + \mu)$, as follows: Let the mth Δn be the difference in wave number between the mth line n_m and the line of next higher frequency; *i.e.*, let

$$\Delta n = n_{m+1} - n_m \tag{3}$$

Since $\Delta n = f(m + \mu)$, we may write the series of equations

$$\left.\begin{aligned} n_{m+1} - n_m &= f(m + \mu) \\ n_{m+2} - n_{m+1} &= f(m + 1 + \mu) \\ n_{m+3} - n_{m+2} &= f(m + 2 + \mu) \\ \vdots \qquad\quad \vdots &\qquad\quad \vdots \\ n_\infty - n_{\infty-1} &= f(\infty - 1 + \mu) \end{aligned}\right\} \tag{4}$$

Adding all of these equations (4), we have

$$n_\infty - n_m = \sum_m^\infty f(m + \mu), \tag{5}$$

where n_∞ is the wave number for very large values of m. We can see from inspection of the two curves in Fig. 71 that, as m

becomes larger, n apparently approaches a limiting value which we may designate, as above, by n_∞. Further, an inspection of Fig. 72 shows that, for large values of m, Δn seems asymptotically to approach zero, and $\sum_m^\infty f(m+\mu)$ is, therefore, probably finite, so that we may put

$$\sum_m^\infty f(m+\mu) = F(m+\mu) \tag{6}$$

where $F(m+\mu)$ is some *other* function of $(m+\mu)$ to be determined. We may, therefore, write equation (5) in the form

$$n_m = n_\infty - F(m+\mu) \tag{7}$$

which is a relation, involving wave numbers, in which n_∞ and μ are constants characteristic of the particular series under consideration, n_∞ being the limiting or *convergent* wave number for the series, and μ being the "shift" constant. The function $F(m+\mu)$ can be determined only by a judicious guess. Rydberg finally concluded that $F(m+\mu)$ must be of the form $N_\infty \cdot (m+\mu)^{-2}$, so that equation (7) becomes

$$n_m = n_\infty - \frac{N_\infty}{(m+\mu)^2} \tag{8}$$

where N_∞ was found to be a universal constant for all series (of this type) for *all substances*, n_∞ and μ being characteristic of each substance. The value of N_∞ may be determined from Balmer's equation, (1),

$$\lambda = h\frac{m^2}{m^2 - a^2}$$

which—in confirmation of Balmer's surmise—is a special case of equation (8). Thus, from equation (1),

$$\frac{1}{\lambda} = n = \frac{1}{h}\left(\frac{m^2 - a^2}{m^2}\right)$$
$$= \frac{1}{h} - \frac{a^2/h}{m^2} \tag{9}$$

which agrees with Rydberg's more general equation if we put

$$\left.\begin{aligned} n_\infty &\equiv \frac{1}{h} \\ \text{and} \qquad N_\infty &\equiv \frac{a^2}{h} = \frac{4}{h} \end{aligned}\right\} \tag{10}$$

since, in Balmer's equation, $a^2 = 4$.

Now, Balmer found that, approximately, $h = 3{,}645.6$ Ångströms, or 0.000036456 cm. In wave numbers and to the same approximation, therefore,

$$N_\infty = \frac{4}{0.000036456} = 109{,}720 \text{ cm.}^{-1}$$

N_∞ is called the "Rydberg (wave number) constant." Because of its great theoretical, as well as numerical, importance, its exact value has been the subject of considerable study. It has been found to vary[1] slightly, from one element to another, the values for hydrogen and helium being, according to Hicks,[2]

For hydrogen .... $N_\infty = 109{,}679.2$
For helium ..... $N_\infty = 109{,}723.6$

in international units.

(*d*) *Numerical Values.*—Rydberg found that the formula

$$n_m = n_\infty - \frac{N_\infty}{(m + \mu)^2}$$

predicted wave lengths very close to the observed ones, although there were small systematic errors. The constants μ and n_∞ for a particular series were determined empirically by the use of tables (see Hicks' "Analysis of Spectra" or Fowler's "Report on Spectral Series"). Thus, for the wave numbers n_d of the successive lines in the diffuse series in sodium shown in Table III, we may use the approximate equation

$$n_d = 24{,}470 - \frac{109{,}675}{(m + 0.987)^2}$$

The series is seen to "converge" for $m = \infty$ at the wave number 24,470.

It has been found that a formula of the Rydberg type but with *three characteristic* constants n_∞, μ, and α, *viz.*,

$$n_m = n_\infty - \frac{N_\infty}{\left(m + \mu + \frac{\alpha}{m}\right)^2} \tag{11}$$

[1] Throughout this chapter, except as otherwise noted, we shall use the symbol N_∞ for the Rydberg constant. We shall see, later (Chap. X), that there are theoretical reasons for the variation of N_∞ with the atomic number of the atom emitting the spectrum. N_∞ will then be used to refer to the value of the Rydberg constant for an atom of theoretically infinite mass compared to the mass of an electron.

[2] "Analysis of Spectra," p. 83.

agrees more closely with experiment. Hicks' "Analysis of Spectra" gives for the long-wave-length component of the diffuse series of doublets of sodium (the same series as is shown in Table III) the formula

$$n_m = 24{,}475.66 - \frac{109{,}675}{\left(m + 0.982390 + \frac{0.013266}{m}\right)^2}$$

This formula predicts the values of the wave lengths of this series within 0.1 Ångström.

The student will find in such excellent books as Hicks' "The Analysis of Spectra" or Fowler's "Report on Series in Line Spectra" a large amount of tabular data on spectral series of the various elements, giving wave lengths, wave numbers, series formulæ, and constants. Such data is well worth careful study, graphical and otherwise, since the interpretation of these series and their relations to the problems of atomic structure are becoming increasingly important.

5. Relations between Series.—It would not serve our purpose to go into great detail with regard to all the various laws of spectral series. We shall call attention to only a few significant relations. In so doing, we shall use the notation given by Fowler,[1] since, for a brief discussion, his notation is more suitable than more recent ones, which can be more profitably employed after we have discussed Bohr's theory of the atom.

(*a*) *Symbols and Notation.*—Rydberg, as we have already mentioned, recognized three types of spectral series, distinguishable from each other by certain physical characteristics, *viz.*, principal, sharp, diffuse. To these were added, later, by the observations of Bergmann and others about 1908, a fourth series which Hicks named the "fundamental series." We may designate these series by the abbreviations, respectively, *P*, *S*, *D*, and *F*. To each of these series a formula of the Rydberg type

$$n_m = n_\infty - \frac{N_\infty}{(m + \mu)^2}$$

applies, at least to a sufficiently close approximation for our discussion.[2]

[1] "Report on Spectral Series."

[2] See, however, equation (11).

We may represent these four series by the respective formulæ

$$P(m) = P_\infty - \frac{N_\infty}{(m + P)^2} \tag{12a}$$

$$S(m) = S_\infty - \frac{N_\infty}{(m + S)^2} \tag{12b}$$

$$D(m) = D_\infty - \frac{N_\infty}{(m + D)^2} \tag{12c}$$

$$F(m) = F_\infty - \frac{N_\infty}{(m + F)^2} \tag{12d}$$

The meaning of the symbols is obvious: For example, in the P series (*i.e.*, the principal series), $P(m)$, P_∞, and P stand, respectively, for n_m, n_∞, and μ of Balmer's general formula. Each of these series may consist of singlets (*i.e.*, single lines) or of doublets or of triplets. For the singlet series, Fowler uses the letters P, S, D, and F, as in equations (12). For the doublet series, he uses the lower-case Greek letters π, σ, δ, and ϕ, with subscripts 1 and 2, to designate the two components of the doublet, subscript 1 being for the stronger (or more intense) component. For triplet systems, he uses the lower-case letters p, s, d, and f, with subscripts 1, 2, and 3. Thus, the formula

$$p_1(m) = p_{1,\infty} - \frac{N_\infty}{(m + p_1)^2} \tag{13}$$

represent the series made up of the first (and strongest) components of a series of triplets. And

$$\delta_2(m) = \delta_{2,\infty} - \frac{N_\infty}{(m + \delta_2)^2} \tag{14}$$

represents the second (and weaker) component of a series of doublets.

A further abbreviation ("shorthand" notation) is effected by writing the terms containing N_∞ as follows:

$$m\delta_2 \equiv \frac{N_\infty}{(m + \delta_2)^2}$$

or,

$$mp_1 \equiv \frac{N_\infty}{(m + p_1)^2}$$

so that, in this abbreviated notation, the equations (13) and (14) become

$$p_1(m) = p_{1,\infty} - mp_1 \tag{13a}$$

$$\delta_2(m) = \delta_{2,\infty} - m\delta_2 \tag{14a}$$

Note that one must distinguish carefully between $p_1(m)$ and mp. The former represents, for the particular values of m, the numbers for the various lines of the series; while the latter is the value of the *term* $N_\infty/(m + p_1)^2$. Thus $p_1(2)$ stands for a particular *line;* it is the strongest line (subscript 1) in the *triplet* (lower-case letter) the value of which is obtained by putting $m = 2$ in the equation for the series. On the contrary, $1p_1$ is the value of the *term* $N_\infty/(m + 1)^2$ which is obtained by letting $m = 1$.

(*b*) *Interrelations between Series.*—The "cross" relations which have been found to exist among the several series in the spectra of a given element effect considerable simplification in the series notation and are indicative of fundamental laws common to the series. These relations are best illustrated by numerical examples:

1. *Convergence frequency of the S (sharp) and the D (diffuse) series.* Fowler gives, for the *P*, *S*, and *D* series[1] of lithium (quoted from Rydberg's work),

$$\left.\begin{aligned} P(m) &= 43{,}488 - \frac{109{,}721.6}{(m + 0.9596)^2}, \quad (m = 1, 2, 3 \cdots) \quad (a) \\ S(m) &= 28{,}601 - \frac{109{,}721.6}{(m + 0.5951)^2}, \quad (m = 2, 3, 4 \cdots) \quad (b) \\ D(m) &= 28{,}599 - \frac{109{,}721.6}{(m + 0.9974)^2}, \quad (m = 2, 3, 4 \cdots) \quad (c) \end{aligned}\right\} \quad (15)$$

The convergent wave numbers of the *S* and the *D* series are seen to be practically identical. That is, in terms of the notation of equations (12),

$$S_\infty = D_\infty \quad (16)$$

2. *Convergence frequency of the P and the S series.* A relation between the *P* and the *S* series is as follows: The value of the variable term for $m = 1$ in either series is, numerically, very nearly the convergence frequency of the *other* series. Thus,

$$\frac{N_\infty}{(1 + 0.9596)^2} = 28{,}573$$

[1] These series for lithium are really close doublets, the separation between the components being of the order of 0.3 of a wave number unit. The lines are so close together that, for our purpose, they may be treated as *singlet* systems; hence the capital letters *P*, *S* and *D*.

and

$$\frac{N_\infty}{(1 + 0.5951)^2} = 43{,}124$$

Now, 28,573 is (nearly) equal to 28,601, the convergence frequency of the S series; and 43,124 is (nearly) equal to 43,488. This agreement is sufficiently good to warrant the law, justified by later work, that

$$\left.\begin{aligned} P_\infty &= \frac{N_\infty}{(1 + S)^2} \quad (a) \\ \text{and} \\ S_\infty &= \frac{N_\infty}{(1 + P)^2} \quad (b) \end{aligned}\right\} \tag{17}$$

Using these relations, equations (16) and (17), we may now rewrite equations (12) as follows:

$$P(m) = \frac{N_\infty}{(1 + S)^2} - \frac{N_\infty}{(m + P)^2} \tag{18a}$$

$$S(m) = \frac{N_\infty}{(1 + P)^2} - \frac{N_\infty}{(m + S)^2} \tag{18b}$$

$$D(m) = \frac{N_\infty}{(1 + P)^2} - \frac{N_\infty}{(m + D)^2} \tag{18c}$$

Or, in the abbreviated notation of equations (13a) and (14a), we may write, instead,

$$P(m) = 1S - mP \tag{19a}$$

$$S(m) = 1P - mS \tag{19b}$$

$$D(m) = 1P - mD \tag{19c}$$

3. *Convergency frequency of the F series.* For the fundamental series in lithium, Fowler gives

$$F(m) = 12{,}203.1 - mF$$

If, in the variable term in the D series, we put $m = 2$, we have

$$\frac{109{,}721.6}{(2 + 0.9974)^2} = 12{,}212$$

which is very nearly equal to 12,203.1, the convergence wave number of the F series. We may, therefore, add to the three equations (18) a fourth,

$$F(m) = \frac{N_\infty}{(2 + D)^2} - \frac{N_\infty}{(m + F)^2} \tag{18d}$$

and to equation (19),

$$F(m) = 2D - mF \tag{19d}$$

4. *Terms.*—The quantities such as $N_\infty/(1+S)^2$ or $N_\infty/(m+P)^2$ on the right-hand side of equations (18) are called the *terms* of the spectral-series formulæ. In the "short hand" notation of equations (19), these terms are referred to, respectively, as the "$1S$" term or the "mP" terms. Since the latter have a multiplicity of values depending on the successive integer values of m, these latter terms are frequently referred to as "sequences." Thus, we have the "mS" sequences given by the successive quantities

$$\frac{N_\infty}{(1+S)^2}, \quad \frac{N_\infty}{(2+S)^2}, \quad \frac{N_\infty}{(3+S)^2} \cdots$$

Each series of lines is given by the *differences* of two *kinds* of terms. For example, the principal series is given by the difference between an S term ($1S$) and the several P terms. Instead of designating a series by a single letter such as P, S, etc., we may, as an alternative symbolism, employ the letters in the two terms which make up the series. For example, the principal series may be called either the P series or the S-P series; similarly, we may designate the sharp, the diffuse, and the fundamental series by, respectively, P-S, P-D, and D-F.

6. The Rydberg-Schuster Law.—From equation (18a), we may write, for the *first line* of the principal series,

$$P(1) = \frac{N_\infty}{(1+S)^2} - \frac{N_\infty}{(1+P)^2} \tag{20}$$

This equation states the Rydberg-Schuster law, announced independently by Rydberg and by Schuster, in 1896, that *the wave number of the first line in the principal series is equal to the difference between the convergence wave number of that series and the common convergence wave number of the S and the D series.*

7. Relations between Doublet Series.—The spectra of the alkali metals, as well as those of several other elements, are characterized mainly by series of doublets. The separations of the components of these doublets follow certain regular rules. Table V gives illustrative data for the first five doublets in the P, the S, and the D series in the spectrum of sodium. An inspection of this table confirms the following conclusions: (1) The differences in wave number between the components of the doublets of both the sharp and the diffuse series, as well as of their respective convergence wave numbers, are constant throughout and are equal to the wave-number difference between

the *first* pair of lines of the principal series. (2) The respective components, first and second, of the sharp and the diffuse series have the *same* convergence wave numbers. (3) The differences in wave numbers between the components in the principal series decrease rapidly for the higher members of the series (*i.e.*, for larger values of m), so that the two principal series have the same convergence frequency.

TABLE V.—DOUBLET SEPARATIONS IN THE SPECTRUM OF SODIUM

Principal series			Sharp series			Diffuse series		
m	Wave number	Δn_π	m	Wave number	Δn_σ	m	Wave number	Δn_δ
1	16,973.35 16,956.17	17.18	2	8,766.34 8,783.13	16.79	2	12,199.48 12,216.64	17.16
2	30,272.86 30,267.37	5.49	3	16,227.37 16,244.54	17.17	3	17,575.30 17,592.47	17.17
3	35,042.66 35,040.17	2.49	4	19,398.34 19,415.51	17.17	4	20,063.20 20,080.34	17.14
4	37,297.70 37,296.20	1.50	5	21,038.37 21,055.55	17.18	5	21,413.73 21,430.89	17.16
5	38,541.54 38,540.07	1.47	6	21,995.00 22,012.18	17.18	6	22,227.11 22,244.25	17.14
∞	41,449.00[1]	.....	∞	24,475.65[2] 24,492.83[3]	17.18	∞	24,475.65[2] 24,492.83[3]	17.18

[1] $41{,}449.00 = \frac{N_\infty}{(1+\sigma)^2}$ [2] $24{,}475.65 = \frac{N_\infty}{(1+\pi_1)^2}$ [3] $24{,}492.83 = \frac{N_\infty}{(1+\pi_2)^2}$

The order of the components of the doublets in the principal series is inverted with respect to the corresponding order for the sharp and the diffuse series. One reason for this is seen by recalling the Rydberg-Schuster law (equation (20)) that the first line of the P series is obtained by subtracting from the convergence wave number of the P series the common convergence wave number of the S and the D series. Since, for doublet series, the two principal series have the *same* convergence frequency, it follows that the component of *greater* wave number in the first P-series doublet will be given by subtracting from the P-series

limit the S and the D limits of *lesser* wave number; and *vice versa*. This inversion of order receives *physical* confirmation from the fact that, in the S and the D doublets, the component of lower wave number (longer wave length) is the stronger; while, in the P doublets, the reverse is the case.

Recalling the cross relations between the P, the S, and the D series given by the equations (18), and remembering that the lower-case Greek letters with suitable subscripts refer to doublet series, we may write the six series for sodium as follows:

$$\text{First principal series } \pi_1(m) = \frac{N_\infty}{(1+\sigma)^2} - \frac{N_\infty}{(m+\pi_1)^2} \tag{21a}$$

$$\text{Second principal series } \pi_2(m) = \frac{N_\infty}{(1+\sigma)^2} - \frac{N_\infty}{(m+\pi_2)^2} \tag{21b}$$

$$\text{First sharp series } \sigma_1(m) = \frac{N_\infty}{(1+\pi_1)^2} - \frac{N_\infty}{(m+\sigma)^2} \tag{21c}$$

$$\text{Second sharp series } \sigma_2(m) = \left[\frac{N_\infty}{(1+\pi_1)^2} + \Delta\sigma\right] - \frac{N_\infty}{(m+\sigma)^2} \tag{21d}$$

$$= \frac{N_\infty}{(1+\pi_2)^2} - \frac{N_\infty}{(m+\sigma)^2} \tag{21d'}$$

$$\text{First diffuse series } \delta_1(m) = \frac{N_\infty}{(1+\pi_1)^2} - \frac{N_\infty}{(m+\delta)^2} \tag{21e}$$

$$\text{Second diffuse series } \delta_2(m) = \left[\frac{N_\infty}{(1+\pi_1)^2} + \Delta\sigma\right] - \frac{N_\infty}{(m+\delta)^2} \tag{21f}$$

$$= \frac{N_\infty}{(1+\pi_2)^2} - \frac{N_\infty}{(m+\delta)^2} \tag{21f'}$$

In equations (21d) and (21f), $\Delta\sigma$ refers to the constant difference in frequency between the components of the sharp and the diffuse doublets.

8. Relations between Triplet Series.—Triplet systems of lines are found in the spectra of the alkaline earth metals—magnesium, calcium, strontium, and barium—and in the spectra of such other elements as zinc, cadmium, and mercury. Singlet systems of lines are, also, found in these spectra. As in the case of doublet series, the systems in each element include the principal, the sharp, and the diffuse groups.

The interrelations among these triplet series are very similar to those found in doublet series: (1) The three principal series converge to the same wave number, which, as in equation (20), is the $1S$ term of the sharp series. (2) The wave-number separa-

tions of the components of the sharp and the diffuse triplets is the same for corresponding components throughout the series. (3) The first sharp and the first diffuse series converge to the wave number given by putting $m = 1$ in the term $N_\infty/(m + p_1)$ of the first principal series. Similar relations hold for the second and the third sharp and the diffuse series. (4) The component of shortest wave length in the principal-series triplets is the stronger. The reverse is the case with the sharp and the diffuse series. These laws are summed up in the following equations, which give, in abbreviated notation, the formulæ for the several series. (Lower-case letters are used for triplets.)

First principal series	$p_1(m) = 1s - mp_1$	(22*a*)
Second principal series	$p_2(m) = 1s - mp_2$	(22*b*)
Third principal series	$p_3(m) = 1s - mp_3$	(22*c*)
First sharp series	$s_1(m) = 1p_1 - ms$	(22*d*)
Second sharp series	$s_2(m) = 1p_2 - ms$	(22*e*)
Third sharp series	$s_3(m) = 1p_3 - ms$	(22*f*)
First diffuse series	$d_1(m) = 1p_1 - md$	(22*g*)
Second diffuse series	$d_2(m) = 1p_2 - md$	(22*h*)
Third diffuse series	$d_3(m) = 1p_3 - md$	(22*i*)

9. Satellites.—The doublets and triplets in the diffuse series are, in many instances, accompanied by "satellites," *i.e.*, faint companion lines. In doublets, one satellite accompanies the component of longer wave length, the satellite being on the long-wave-length side, and the line itself being displaced slightly toward shorter wave lengths, which displacement, however, decreases with higher orders of the line (*i.e.*, larger values of m). In triplets, the long-wave-length component has *two* satellites; the middle component has one; and the short-wave-length component, none. These satellites make the lines appear diffuse at low dispersion. We shall see, later, that these satellites play a very fundamental role in the theory of spectra.

10. Combination Lines.—The formulæ, such as equations (21) and (22), which have been found to express the wave numbers of series of lines are all seen to give the wave number of any given line by means of the *difference* between two *terms*. These terms are, for a given series, a *fixed* term, called the "limit of the series" and a *variable* term the values of which depend on the integer values of m. The fixed term, or limit, of a given series is obtained by putting $m = 1$ (or $m = 2$ for the fundamental F series) in the

variable term of *some other series.* Thus, the second principal series, say of sodium, is given by (equation (21*b*))

$$\pi_2(m) = \frac{N_\infty}{(1+\sigma)^2} - \frac{N_\infty}{(m+\pi_2)^2} \qquad (21b)$$

The first term on the right is the variable term of the sharp series with $m = 1$.

It occurred to Rydberg, the actual discovery *being made later*[1] by Ritz, that other combinations of terms than those giving the four chief series might correspond to spectral lines observed to be present in spectra but not belonging to the series. Thus, if the difference in the two terms

$$\frac{N_\infty}{(1+\sigma)^2} - \frac{N_\infty}{(1+\pi_2)^2}$$

gives the first line of the second principal series, one might predict a line by taking the difference between such terms as

$$\frac{N_\infty}{(2+\sigma)^2} - \frac{N_\infty}{(3+\pi_2)^2}$$

Indeed, one might get a whole series of such lines with the first term $N_\infty/(2+\sigma)^2$ as the convergence limit and the second term as the variable term of such a series, replacing the integer 3 by 4, 5, 6 . . . in turn. Such lines, or series, are actually found to exist and are called *combination lines* or *series.* Thus, in the infra-red spectrum of sodium is found a line $\lambda = 3.418\mu$, wave number 2,925. The wave number of this line is given by the difference between the terms

$$\frac{N_\infty}{(2+\pi_1)^2} - \frac{N_\infty}{(3+\sigma)^2}$$

$$(11{,}175 - 8{,}248 = 2{,}927)$$

Many other such "combination" lines are found in spectra.

11. The Significance of Spectral-series Terms.—These combination lines serve to emphasize the fact that in spectral series the *terms* are the fundamental quantities; that to any given atom belongs a *multiplicity* of such terms, the wave numbers of the lines emitted by the atom being given by the *differences* between *pairs* of terms. Now, multiplying wave number n by c, the velocity of light, gives frequency ν, *i.e.*, $nc = \nu$; and, therefore,

$$h \cdot nc = h\nu$$

[1] *Astrophys. Jour.*, vol. 28, p. 237 (1908).

where h is Planck's constant. The product $h\nu$, as we have seen, in Chap. VII, represents a *quantity of energy*, or a *quantum*. Accordingly, if a formula for a spectral line, such as

$$\pi_2(3) = \frac{N_\infty}{(1+\sigma)^2} - \frac{N_\infty}{(3+\pi_2)^2} \tag{22}$$

be multiplied through by ch, *viz.*,

$$ch \cdot \pi_2(3) = ch\frac{N_\infty}{(1+\sigma)^2} - ch\frac{N_\infty}{(3+\pi_2)^2} \tag{23}$$

the quantity on the left-hand side becomes a *quantum of energy* corresponding to the frequency ν of the emitted line, in this particular illustration the long wave-length component of the third doublet in the principal series, say, of sodium, the wave number of which (see Table V) is 35,040.17. This wave number, multiplied by ch gives

$$35{,}040.17 \times 2.998 \cdot 10^{10} \times 6.554 \cdot 10^{-27} = 6.885 \cdot 10^{-12} \text{ ergs}$$

Whatever the actual numerical magnitudes of the two terms on the *right*-hand side of equation (23), they must be *quantities of energy*, say W_1 and W_2, respectively, such that their *difference* is, for this particular line, equal to 6.885×10^{-12} ergs. Or, to generalize, *we may write equations of the type of equation* (23) *in the form*

$$h\nu = W_1 - W_2 \tag{24}$$

This equation is *a generalization from the empirical data on line spectra extended by aid of Planck's quantum hypothesis.* These data, however, give us no clue whatever to the *interpretation* of the equation in terms of more fundamental relations. It remained for Bohr to give an interpretation of this equation in his theory of atomic structure and the origin of spectra, to which we shall turn in Chap. X.

Independently of Bohr's theory, however, we may remark that the numerical significance of equation (24) is quite unambiguous: The quantum of energy $h\nu$ corresponding to a spectral line of frequency ν is equal to the *difference* between two energy terms W_1 and W_2 the *numerical values of which are computable from the terms in the spectral-series equations, by multiplying these terms by* $c \cdot h$. Indeed, we may speculate a little farther into the deeper meaning of the quantities W_1 and W_2 on the basis of the law of the conservation of energy. When an atom radiates it emits energy. This energy must come from energy previously

stored in the atom. We may, therefore, think of W_1 as a certain amount of energy so stored. As a result of some atomic "catastrophy," the energy of the atom "drops" to W_2, and an amount of energy $h\nu$ equal to the difference $(W_1 - W_2)$ is emitted. *We reach these conclusions without the necessity of making further postulates as to the nature of radiation or as to the atomic mechanism involved in the process.*

12. Spectral Series and Atomic Properties.—(*a*) Numerous attempts have been made to establish numerical relations between the various spectral series and the several properties

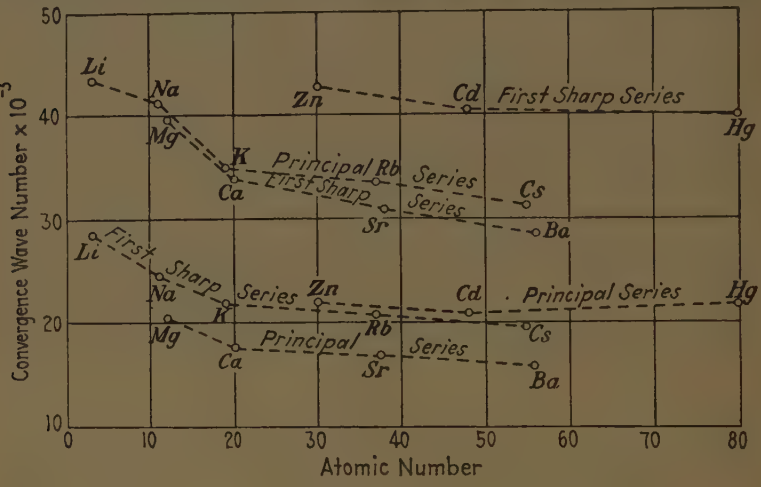

FIG. 73.—Relation between convergence wave numbers of several series and atomic number.

of the respective atoms in which they originate, as, for example, atomic weight, atomic volume, atomic number, etc. Evidence of the probable existence of such relations comes from several sources: (1) The fact that the Rydberg constant N_∞ appears, with only slight variation in value, in all spectral series of the type discussed above is evidence of *something* common to all series of this type, irrespective of the atoms from which they originate; *i.e.*, N_∞ must be very intimately connected with the energy quantities W_1 and W_2 of equation (24). (2) The spectra of elements of a given group in the periodic table are made up of similar multiplets. For example, the spectra of the alkali metals consists of doublets, comparatively close together; of the alkaline earths, triplets and singlets. (3) The very fact that

spectral-series formulæ of the same type are applicable to the spectra of many different elements is itself suggestive.

(*b*) Some examples of the way in which atomic properties affect spectral series are given in Table VI and are shown graphically in Figs. 73, 74, and 75. Figures 73 and 74 show the convergence wave numbers of the principal and of the first sharp series as functions, respectively, of the atomic number and the atomic volume. In Fig. 73, it is observed that, although there is, in general, a decrease in the series limits of any one group of elements with increasing atomic number, with the possible exception of the principal series of the group Zn, Cd, and Hg, this decrease follows no regular law.

TABLE VI.—SERIES LIMITS AS FUNCTIONS OF ATOMIC NUMBER AND ATOMIC VOLUME

Element	Atomic number	Atomic volume[1]	Series limits		Doublet separation	
			Principal	First sharp		
Li	3	13.1	43,486	28,582	0.3	
Na	11	23.7	41,449	24,476	17.2	
K	19	45.5	35,006	21,963	57.9	
Rb	37	55.8	33,689	20,872	236.0	
Cs	55	70.0	31,405	19,672	553.9	
					Triplet separations	
					$_1\Delta n_2$	$_2\Delta n_3$
Mg	12	14.0	20,474	39,760	40.5	20
Ca	20	25.9	17,765	33,989	105	52.5
Sr	38	33.7	16,898	31,038	394	187
Ba	56	39.2	15,869	28,515	878	370
Zn	30	3.76	22,094	42,876		
Cd	48	13.1	21,054	40,711		
Hg	80	14.2	21,830	40,138		

[1] Cubic centimeters per gram-atom. Data from International Critical Tables.

It was suggested by Halm[1] that there might be a possible relation between series limits and atomic volume. Figure 74 shows the same series limits as Fig. 73 but plotted against atomic volume instead of against atomic number, as in the latter figure.

[1] *Trans. Roy. Soc. Edinburgh*, vol. 41, p. 593 (1905).

A comparison of the two figures shows that, so far as regularity is concerned, there is little to choose between the two methods of plotting.

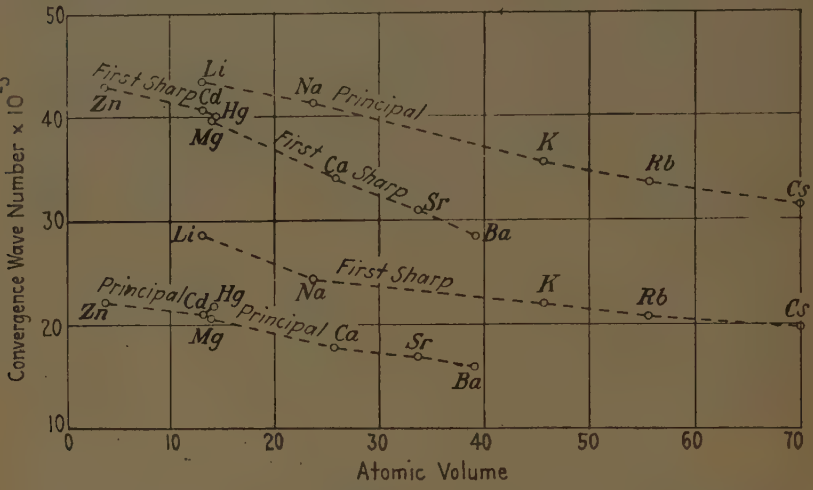

FIG. 74.—Relation between convergence wave number of several series and atomic volume.

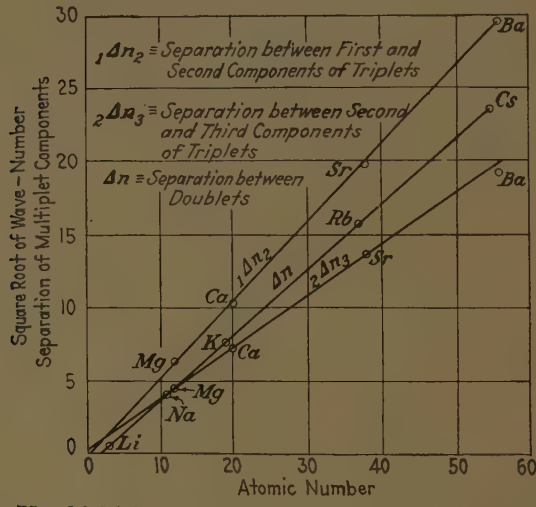

FIG. 75.—Multiplet separation as a function of atomic number.

(*c*) The separations of the components of doublets and triplets follows a much more regular law. Data for the difference in wave numbers between the doublets in the sharp and the diffuse

series of the alkali metals and between the first and second and the second and third components of the triplets of the alkaline earth metals are included in Table VI. These relations are shown graphically in Fig. 75, in which $\sqrt{\Delta n}$ is plotted as a function of atomic number. The linear relation between $\sqrt{\Delta n}$ and atomic number is seen to be quite exact in the case of the alkali metals and only slightly less so for the triplet separations in the other group of elements. Hence, we have the approximate law *that the square roots of the separations between the corresponding components of doublets or triplets is proportional to the atomic number.*

(*c*) *Comparison of Spectral-series Formulæ with the Formula for the Hydrogen Spectrum.*—Let us return, for a moment, to the formula for the Balmer's series in the spectrum of hydrogen. Equation (9), *viz.*,

$$n = \frac{1}{h} - \frac{a^2/h}{m^2} \qquad [9]$$

may be put in the form

$$n = \frac{N_\infty}{a^2} - \frac{N_\infty}{m^2} \qquad (27)$$

remembering that $N_\infty = a^2/h$. For the Balmer's series, a has the value 2, and m takes on the successive values 3, 4, 5 . . . This equation is seen to be a special case of the Rydberg type of formula, such as, for example (equation (18*b*)),

$$S(m) = \frac{N_\infty}{(1+P)^2} - \frac{N_\infty}{(m+S)^2}, \qquad [18b]$$

since, in equation (27), the denominators of the *terms* are integers, instead of integers plus decimal fractions, such as P or S, in equation (18*b*). As a matter of fact, equation (27) is only a very close approximation, since more accurate observations since Balmer's time have shown that the Balmer's series in hydrogen is more accurately represented[1] by the equation

$$n = \frac{N_\infty}{(2 - 0.00000383)^2} - \frac{N_\infty}{(m + 0.00000210)^2} \qquad (28)$$

where

$$N_\infty = 109{,}678.28$$

Neglecting these small decimals, however, we may say that the denominators of both *terms* in Balmer's equation are integers,

[1] FOWLER'S Report, p. 89.

in contrast to Rydberg's general type of equation. We may now, in passing, point out two important relations between Balmer's equation for hydrogen and the more general equations:

1. For large values of m (terms of high order), the terms of the Rydberg type of formula approach the value of the corresponding term (*i.e.*, for the same value of m) of the Balmer formula for hydrogen, since for such large values of m the decimal fractions, such as P and S, become *relatively* less important. This means that for large values of m spectral terms in general become more "hydrogen like."
2. Corresponding terms in the respective series become, in general, more "hydrogen like" in the order S, P, D, F. This is illustrated by the following data[1] for the terms for $m = 3$ in the several series in lithium:

$$S \text{ series: } \frac{N_\infty}{(3+\sigma)^2} = \frac{N_\infty}{(3.5976)^2}$$

$$P \text{ series: } \frac{N_\infty}{(3+\pi_1)^2} = \frac{N_\infty}{(3.9540)^2}$$

$$D \text{ series: } \frac{N_\infty}{(3+\delta)^2} = \frac{N_\infty}{(3.9978)^2}$$

$$F \text{ series: } \frac{N_\infty}{(3+\phi)^2} = \frac{N_\infty}{(3.9998)^2}$$

The denominators under N_∞ are seen to approach more nearly the integer 4 in the order S, P, D, F.

We shall have occasion to refer to these relations later.

13. Enhanced or Spark Spectra.—The series of lines considered in the preceding sections are made up, for the most part, of the lines appearing in the arc or flame spectra of the elements. When the excitation is more intense, as, for example, when the excitation is produced by a high-voltage condenser discharge, additional lines appear in the spectrum of many elements, such as helium and the alkaline earths. Because of the method of production, these lines were called "spark" lines or "enhanced" lines.

Series relationships have, in many cases, been established among these spark lines. Such series are similar to those discussed above, except that, instead of the Rydberg constant N_∞,

[1] Computed from tables in HICKS' "Analysis of Spectra," p. 316.

the constant (very nearly) $4N_\infty$ is used. Thus, in the spark spectrum of helium are three series of lines represented by the formula (very similar to Balmer's formula for hydrogen, equation (27))

$$n = 4N_{He}\left(\frac{1}{a^2} - \frac{1}{m^2}\right) \tag{29}$$

in which, according to Fowler, $N_{He} = 109{,}723.22$. The first four lines of each of these three series are given in Table VII.[1]

TABLE VII.—SERIES OF ENHANCED LINES IN THE SPARK SPECTRUM OF HELIUM

Lyman series: $n = 4N_{He}\left(\frac{1}{a^2} - \frac{1}{m^2}\right)$ where $a = 2$		
$m = 3$	$\lambda = 1{,}640.2\ A$	$n = 60{,}968$
4	1,216.0	82,237
5	1,084.9	92,174
6	1,026.0	97,466
"4,686" series: $n = 4N_{He}\left(\frac{1}{a^2} - \frac{1}{m^2}\right)$ where $a = 3$		
$m = 4$	$\lambda = 4{,}685.6\ A$	$n = 21{,}334$
5	3,203.3	31,209
6	2,733.3	36,575
7	2,511.3	39,808
Pickering series: $n = 4N_{He}\left(\frac{1}{a^2} - \frac{1}{m^2}\right)$ where $a = 4$		
$m = 5$	$\lambda =$ —	$n =$ —
6	6,560.4	15,239
7	5,411.7	18,474
8	4,859.5	25,573

In the alkaline earth group are found series of spark lines involving the constant $4N_\infty$, which correspond to the four main series, *P*, *S*, *D*, and *F*, of arc spectra. The arc spectra of these elements are triplets and singlets. Their spark spectra, however, are made up of *doublets*, similar to the spectra of the alkali metals which constitute the *preceding* group in the periodic table.

[1] Data taken from FOWLER'S "Report on Series in Line Spectra."

As an illustration, Fowler gives for the longer-wave-length component of the sharp series of *doublets* in the *spark* spectrum of calcium a formula of the Hicks type, *viz.*,

$$\sigma_1(m) = 70{,}325.29 - \frac{4N_\infty}{\left(m + 1.205543 - \dfrac{0.064899}{m}\right)^2}$$

Doublet differences in these spark spectra show the same characteristics as in arc spectra; *i.e.*, the doublet separations in sharp and diffuse doublets are constant for a given element and are equal to the doublet separation in the first pair of the principal series.

We shall discover a ready explanation of these series of spark lines in the discussion of Bohr's theory, and we shall see that, by very intense spark discharges, series involving still higher multiples of N_∞ can be produced.

14. Band Spectra.—If one looks at the spectrum of the carbon arc with a spectroscope of moderate resolving power, one will observe, at the extreme (violet) edge of the visible part of the spectrum, "bands," or very broad lines, which are sharply defined and brightest on the long-wave-length edge, and which fade out gradually toward shorter wave lengths. With higher resolving power, these "bands" are seen to be composed of a large number of lines which are crowded together at the long-wave-length edge, called the "head" of the band, and are separated farther and farther toward the short-wave-length side, the lines, however, being so close together as to appear, under low resolving power, like a *continuous* spectrum.

It will not be profitable to go into detail at this point with regard to the large amount of very complex empirical data on the band spectra of various substances. In general, several band edges or heads are found grouped together in a regular sequence, as in the violet bands in the carbon arc, and these constitute a *group* of bands. Several related *groups* form a system of bands. And a given spectrum may contain several such *systems*. Three classes of bands are now recognized: (*a*) bands in the extreme infra-red part of the spectrum, called, from the present theory of their production, "rotation" bands; (*b*) another class, usually found in the near infra-red, called "rotation-vibration" bands; and a third class (*c*) found in the ultra-violet or, in some cases, in the visible, called "electronic" bands.

The series formulæ for band spectra are quite different, *algebraically*, from the formulæ of the Balmer-Rydberg type which we have discussed in Sec. 4. For example, Deslandres[1] found that a formula of the type

$$n = A + bm^2 \tag{30}$$

($n \equiv$ wave number; $b \equiv$ a constant characteristic of the band; $A \equiv$ the wave number of the "head" of the band; and $m = 1, 2, 3 \ldots$) gives an approximation to the wave numbers of lines of certain bands. Thus, in the spectrum of nitrogen is a band with a head at $\lambda = 3914.6A$ the lines of which, according to Baly,[2] can be represented by the formula

$$n = 2554.54 + 0.015335(m - 1)^2 \tag{31}$$

as is shown by Table VIII.

TABLE VIII.—THE "3914.6" BAND IN NITROGEN; WAVE NUMBERS BOTH AS OBSERVED AND AS COMPUTED FROM EQUATION (31)

m	Wave number, n	
	Observed	Computed
1	2554.54	2554.54
10	2555.78	2555.78
23	2561.97	2561.96
39	2576.72	2576.68
55	2599.16	2599.26
63	2613.08	2613.49

We shall refer to band spectra again, very briefly, at the end of Chap. X. The mechanism involved in the production of the band spectrum of a substance is not so different from that giving rise to the spectra of the Balmer-Rydberg type as the difference in the formulæ might suggest. Band spectra arise from molecules; the Balmer-Rydberg spectra, from atoms.

15. Effect of External Physical Conditions on Spectral Lines.—The frequencies of spectral lines are only slightly affected by external physical influences. Such effects, though small, are of considerable importance. We shall make very brief mention of a few of these effects, some of which we shall consider later.

[1] *Compt. rend.*, 1885 to 1904.

[2] BALY, E. C. C.: "Spectroscopy."

(*a*) *The Zeeman Effect.*—We have already discussed, in Chap. VI, the Zeeman effect, namely, the splitting up of a spectral line into components when the source is placed in a strong magnetic field. In the so-called *normal* Zeeman effect, the line is split up into a triplet. The Zeeman effect in most spectral lines, however, is *abnormal*, in that *more* than three components are observed. Although there are great differences among series, the lines of a *given* series usually behave in a similar way as regards their Zeeman patterns. This fact is of some little assistance in identifying lines in series.

We saw, in Chap. VI (equation (19)) that the classical theory of the Zeeman effect gave the change in frequency $\Delta\nu$ when the emitting source is in a field of strength H, as (e is expressed here in electrostatic units)

$$\Delta\nu = \frac{He}{4\pi mc} \tag{32}$$

If Δn_H denotes the wave-number (instead of frequency) shift in a field of strength H, we may write,

$$\frac{\Delta n_H}{H} = \frac{\Delta\nu}{H \cdot c} = \frac{e}{4\pi mc^2} = a \tag{33}$$

where a is a universal constant.

Accordingly, $\Delta n_H/H$, the Zeeman shift in wave number per gauss, should be constant for all values of H. This constancy has been confirmed by experiment, and the value of a, *i.e.*, the shift per gauss for the so-called "normal" triplet, to which equation (32) applies, has been found *experimentally* to be

$$a = 4.692 \times 10^{-5} \text{ wave number per gauss}$$

Theory gives 4.70×10^{-5}, by putting the numerical values of e, c and m in equation (33).

The classical theory, however, fails *completely* to account for the *abnormal* Zeeman effect, in spite of the fact that, *as we saw in Chap. VI, the success of classical theory in explaining the normal Zeeman effect and in deriving therefrom the correct value of e/m was one of the very strong supports for the existence of the electron.* The main experimental facts of the abnormal Zeeman effects are simply stated: (1) The number of components, instead of being three, as in the normal effect, may be four or more depending on the line. (2) The shift of any component is proportional to H and is a simple *submultiple* of the quantity a of equation (33). (3) The "pattern" is symmetrical both as to number, distribu-

tion, and intensity of lines, about the position of the line in zero field.

As an example of an abnormal Zeeman pattern may be taken the neon line[1] $\lambda = 6678A$. This is a "nonet" (nine components when viewed *transversely* to the field). The distribution of these nine components is shown on a wave-number scale in Fig. 76(a), zero of the scale corresponding to the unshifted position of the line. The relative intensities of the respective components are given by the numbers immediately above the lines. The three lines comprising the central group are plane polarized in a direction *parallel* to the magnetic field and are spoken of as[2] π components. The groups of three at the ends are plane polarized in a direction *at right angles* to the direction of the field. These are called σ components. Figure 76(b) shows a conventional diagram

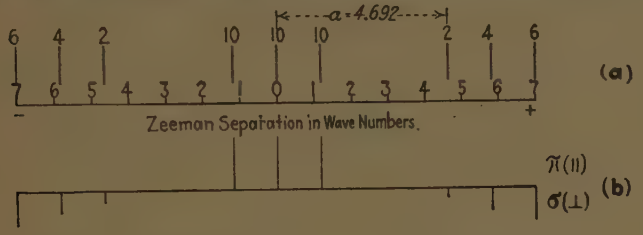

FIG. 76.—The Zeeman pattern of the neon line, $\lambda = 6678A$.

for representing both the polarization and intensity of the lines. In this diagram, the lengths of the lines are proportional to their respective intensities, and the π components are plotted above the horizontal line; the σ components, below.

The normal separation $a = 4.692$ wave numbers, as required by classical theory, is shown above (Fig. 76(a)). The outside lines of the *central* group are displaced exactly $\frac{1}{4}a$ from zero. The end components are displaced $\pm a$, $\pm\frac{5}{4}a$, and $\pm\frac{6}{4}a$ from zero. In other words, the separations are all multiples of $a/4$.

All these facts are conventionally included in the mnemonic notation:

$$\frac{-1 \cdot 0 \cdot 1}{-6 \cdot -5 \cdot -4 : 4 \cdot 5 \cdot 6}\,4$$

[1] Quoted by HICKS, "Analysis of Spectra," p. 92.

[2] π and σ, as here used, are not to be confused with π and σ as used to designate series of doublet lines in the Fowler notation for spectral series. The new series notation does not use Greek letters. Hence, the use of π and σ, as applied to components in the Zeeman effect, is permissible.

the "$-1 \cdot 0 \cdot 1$" above the line indicating that there are three π components, and "$-6 \cdot -5 \cdot -4 : 4 \cdot 5 \cdot 6$" below the line indicating that there are six σ components, the numbers, in each case, giving the displacements of the lines from the zero position in $\frac{1}{4}a$, the "4" at the end of the line indicating the fraction of "a." In a similar notation for intensities, we may write,

$$\frac{10 \cdot 10 \cdot 10}{6 \cdot 4 \cdot 2 \cdot 2 \cdot 4 \cdot 6}$$

Since the pattern is perfectly symmetrical, we may omit the negative displacements and the corresponding intensities and write, for the Zeeman pattern,

$$\frac{0 \cdot 1}{4 \cdot 5 \cdot 6} 4 \frac{(10 \cdot 10)}{(2 \cdot 4 \cdot 6)} \qquad (34)$$

the numbers within the bracket standing for intensities. There are numerous variations of this notation. Thus, we may write for this pattern,

$$0 \cdot 1/4 \cdot 5 \cdot 6/4\ (10 \cdot 10/2 \cdot 4 \cdot 6) \qquad (35)$$

Table IX, compiled from Hicks' "Analysis of Spectra," gives the Zeeman patterns of a number of representative lines. Note that the lines given in the table for Na, K, Cu, and Mg, although, in each case, components of multiplets, have *different* Zeeman patterns.

TABLE IX.—ZEEMAN PATTERNS OF SOME REPRESENTATIVE LINES
(Compiled from Hicks' "Analysis of Spectra")

Element	Wave length of "line"	Zeeman pattern	
He	5015.73*A*	0/1/1	Normal triplet
He	4437.72	0/1/1	Normal triplet
Li	6707.84	0/1/1	Normal triplet
Na	5889.96	1/5 · 3/3	Sextet
	5895.93	2/4/3	Quadruplet
K	4044.14	1/5 · 3/3	Sextet
	4047.20	2/4/3	Quadruplet
Cu	3247.65	1/5 · 3/3	Sextet
	3274.06	2/4/3	Quadruplet
Mg	3838.28	0 · 1/1 · 2 · 3/2	Nonet
	3832.31	1 · 2/0 · 1 · 3/2	Nonet
	3829.36	0 · 2/0 · 2 · 4/2	Octet
Hg	5460.74	0 · 1/2 · 3 · 4/2	Nonet
Hg	3663.27	3 · 6/4 · 7 · 10 · 13/7	Twelve components
Cr	5208	0 · 1 · 2/3 · 4 · 5 · 6 · 7/6	Fifteen components

(*b*) *Stark Effect.*—An effect of an electric field, somewhat analogous to the Zeeman effect, was discovered by Stark, in 1913, and is known as the "Stark effect." It is observed in the well-known "canal rays," when these are moving in an electric field of several thousand volts per centimeter. The arrangement for producing the Stark effect is shown diagrammatically in Fig. 77. *A* and *C* are, respectively, the anode and cathode in a glass tube, the gas in which may be maintained at such a pressure that the Crookes' dark space in front of *C* is several centimeters long. *C* is perforated with small holes through which pass in cylindrical bundles luminous streams of atoms of the gas which have acquired a positive charge immediately in front of *C*. These streams of atoms are the canal rays. A third terminal *S* is placed immedi-

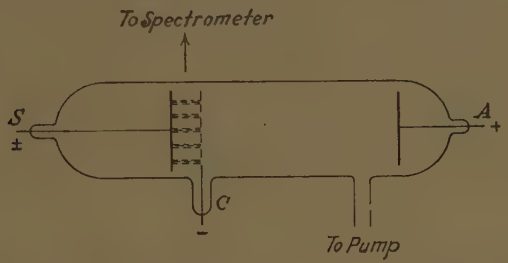

FIG. 77.—Schematic arrangement for producing the Stark effect.

ately behind *C*, at a distance of a few millimeters, and an electric field of several thousand (20,000 and up) volts per centimeter is maintained between *S* and *C*. For the "transverse" Stark effect, light from the canal rays enters the spectroscope in the direction of the arrow. Stark observed that the lines in the spectrum emitted by the canal rays when no field exists between *S* and *C*, are split up, when the field is applied, into numerous components somewhat after the manner of the Zeeman effect, the lines being polarized, some of them parallel to the field (*p* components), others perpendicular (*s* components).

Using the same type of notation as in the Zeeman effect, but expressing the displacements from the zero position of the line directly in wave numbers (instead of in rational submultiples of some such "normal" displacement as applies to the Zeeman effect), the Stark pattern for the hydrogen line H_β ($\lambda = 4861.33A$)

in a field of some 30,000 volts per centimeter is made up of six components, as follows:

$$\frac{-4.01 \cdot +0.89 \cdot +4.18\ (p)}{-2.14 \cdot +0.89 \cdot +2.23\ (s)} \left(\frac{(7 \cdot 1 \cdot 10)}{(6 \cdot 1 \cdot 8)}\right)$$

The three numbers above the line indicate the position of the three components polarized parallel (p) to the field, and the three numbers below the line indicate perpendicularly (s) polarized components. The numbers within brackets indicate relative intensities. It is observed that the pattern is not symmetrical about the zero position. In very strong fields (75,000 volts per centimeter), the pattern changes completely: the number of components is greatly increased, and there is symmetry about the zero position both as to the position of the components and their intensities. Hicks ("Analysis of Spectra," pp. 102–109) gives examples of various Stark patterns.

Classical theory fails to account for the Stark effect. The quantum theory has been more successful.

(*c*) *Temperature.*—The Zeeman effect and the Stark effect are changes produced in the actual frequency of the atomic radiating mechanism itself. The *observed* frequency of a spectral line, however, may be slightly changed by the motion of the radiating atom in the line of sight, on account of Doppler's principle: the apparent frequency *increasing* if the motion is *toward* the observer and *decreasing* if the motion is *away* from the observer. As is well known, the measurement of the radial velocity of stars is based on this principle.

In a luminous gas, such as the mercury vapor in the mercury arc lamp, the atoms are moving with a Maxwellian distribution of velocity, the average velocity increasing with temperature. The *apparent* frequency of the radiation emitted by a given atom at a particular instant when it has a component of velocity, due to temperature agitation, *away from* the observer, will be slightly less than the actual frequency, the difference between the actual frequency, and the observed frequency increasing with increase in this component velocity. Only for those atoms which have no component of velocity in the direction of the observer will the *observed* frequency of the emitted light be equal to the actual frequency.

It is readily seen, therefore, that a spectral line emitted by a gas comprises, as observed, a *range* of frequencies *symmetrically*

distributed about the *true* frequency of vibration for the atom at rest; and, further, that this range should increase with increasing temperature. In short, the *breadth* of a spectral line should depend on the temperature of the source: the higher the temperature the broader the line. The distribution of intensity throughout the width of the (observed) line is determined by Maxwell's *distribution of velocities*. According to Rayleigh,[1] the brightness of the line at a distance $\pm \Delta n$ wave numbers from the center is proportional to

$$e^{-k \cdot \overline{\Delta n}^2}$$

where k is a constant which depends on the temperature and on the mass of atom, and e is the Naperian base of logarithms.

Michelson[2] has studied the width of spectral lines by the interferometer method. He found that at low gas pressures the breadth of the line, as observed experimentally, agrees with that computed from Doppler's principle and Maxwell's distribution law. Subsequently, Fabry and Buisson,[3] using the interferometer method, investigated the breadth of lines in the spectra of the rare gases. They confirmed the formula that the breadth Δ of a line of wave length λ should be

$$\Delta = 0.82 \times 10^{-6} \lambda \cdot \sqrt{\frac{T}{m}}$$

where T is the absolute temperature and m is the atomic weight or molecular weight of the "luminous particle." At liquid-air temperatures, the breadth of the krypton line $\lambda = 5570$ A was found to be only 0.006 A, of which breadth practically all could be ascribed to the Doppler effect resulting from thermal agitation at that temperature. When we realize that a very large number of atoms "cooperate" in the production of any single line as we see it (or photograph it) in the spectroscope and that, nevertheless, except for the Doppler effect, the frequencies emitted by these several atoms *are identical within the very high limits of resolution of spectroscopic apparatus*, we see that the atom must be a thing of great definiteness, at least so far as concerns the frequency of the characteristic radiation which it emits

[1] *Phil. Mag.*, vol. 27, p. 298 (1889).

[2] *Phil. Mag.*, vol. 34, p. 280 (1892); *Astrophys. Jour.*, vol. 3, p. 251 (1896). See, also, DRUDE: "Theory of Optics" (translation by Mann and Millikan), p. 537.

[3] *Jour. phys.*, vol. 2, p. 442 (1912).

(*d*) *Pressure.*—From the fact that, under favorable conditions, interference fringes can be produced in an interferometer when the difference in the path of the two beams is as much as several hundred thousand wave lengths, it is inferred that the wave train sent out by any particular atom is continuous, *i.e.*, is without change of phase, for at least that number of vibrations. In order that the atom may emit wave trains of this length, it must be "free from interruptions" for a corresponding period of time. In the terminology of the kinetic theory of gases, this means that the *mean free time* between collisions with other atoms must, on the average, exceed the time required to emit a complete wave train, since it may be assumed that a collision with another atom would cause either a change of phase or excessive damping or other disturbance.

Now, collisions between atoms become more frequent the higher the pressure, for a given temperature, of the gas. The higher the pressure the shorter, therefore, should be the wave trains, and the more frequent the abrupt changes of phase. Houstoun[1] has shown that "a train of sine waves with a constant period but irregular changes of phase is equivalent to the superposition of a number of perfectly regular trains, the periods of which differ slightly from the period of the irregular train." In short, at higher gas pressure, not only should there be a broadening of the line due to the Doppler effect but also an additional broadening due to the increasing frequency of phase changes resulting from collisions. Michelson has confirmed this by showing, by measurements with the interferometer, that below a pressure of the order of a millimeter, the breadth of the hydrogen line $\lambda = 6563A$ is almost entirely due to the Doppler effect; but that at higher pressures, the line becomes considerably broader.

The picture of the atom and its vibrating mechanism, which one has in mind in considering, as above, the effect of temperature and pressure on the width of the spectral lines, *is more or less definitely based upon the classical concept of the emission of radiation in long wave trains.* Indeed, we might regard the explanation of these comparatively minute effects *as a final triumph of classical theory.* These effects can be explained by the quantum theory,

[1] "A Treatise on Light," Chap. XXI.

but the quantum theory suggests *no picture* of the radiating mechanism involved.

In this chapter, we have presented a brief outline of some of the experimental facts connected with the characteristic line spectra of the atoms and molecules. We have limited the discussion to the visible and the near-visible region of the spectrum, omitting, for example, all reference to X-ray spectra, since the latter can best be presented in connection with a consecutive discussion of X-ray phenomena (Chap. XII). We have seen that the data are very complex: that a given atom may emit hundreds or even thousands of lines, each line involving a perfectly definite, sharply defined, frequency. We have seen that the relation between the frequencies of the various lines in the spectrum of a given element are such as to preclude the possibility of their arising from a fundamental frequency and its overtones. Classical physics could picture no atomic mechanism composed of electrons and positive charges and capable of vibrating in so many different modes. In characteristic line spectra, as in temperature radiation, the quantum theory succeeded, when the classical theory failed.

CHAPTER X

THE NUCLEAR ATOM AND THE ORIGIN OF SPECTRAL LINES

The atomic model proposed by Bohr, in 1913, and now known as the "Rutherford-Bohr atom model" or, more briefly, as the "nuclear atom," was the result of a gradual evolution of ideas, which extended over several decades and to which many different investigators contributed. A bird's-eye view of the speculations on atomic structure preceding the work of Rutherford and of Bohr will assist the reader in appreciating fully the revolutionary nature of the concepts introduced by these two scientists.

1. Early Views on Atomic Structure.—Speculations as to the structure of the atom probably date from the work of Dalton, in the early years of the nineteenth century. Dalton showed that chemical combinations between substances always take place in definite proportions—a fact which could be accounted for by assuming that each elementary substance is composed of *atoms*. Once the *existence* of atoms was rendered probable, it was natural to speculate about their *structure*.

In 1815, Prout proposed the hypothesis which bears his name and which asserts that *all elements are made up of the atoms of hydrogen as a primordial substance*, since the atomic weights of a large number of the elements are very nearly simple multiples of that of hydrogen. Prout had no further data to support his views other than the circumstantial evidence coming from atomic weights. Accordingly, when more accurate determinations showed that, in general, atomic weights were *not* exact integer multiples of the atomic weight of hydrogen and that there were such notable exceptions as chlorine, atomic weight 35.5, Prout's hypothesis was abandoned—only to be revived again decades later in a new form and, of course, on the basis of newly discovered *experimental* evidence (see Chap. XIII).

The first real foundations upon which our modern theories of atomic structure are being built were laid by Faraday, about 1835, when he enunciated the laws of electrolysis and thereby

made it clear that with each univalent atom taking part in electrolysis is associated a definite electric charge, or multiple thereof for a multivalent atom, which is the same for *all* atoms. We have previously discussed (Chap. VI) the development of the concept of the electrical nature of matter, which culminated in the discovery of the electron by Sir J. J. Thomson, in 1897. Therewith, theories of atomic structure began to assume a more definite form, since it then became obvious that the atom must be made up of numerically equal quantities of negative and of positive charges and that practically the entire mass of the atom must be associated with the positive charge.

2. The Thomson Atom.[1] (*a*) *The Number of Electrons per Atom.*—When, following the discovery of the electron, it became evident that electrons were constituent parts of all atoms, there arose two questions of importance: (1) How many electrons are there in atoms? and (2) How are the electrons and the positive charges in the atom arranged? Three more or less independent lines of evidence gave an answer to the first of these two questions:

1. On the basis of classical theory, Sir J. J. Thomson showed that, when a beam of X-rays passes through matter, it should be scattered, the scattering coefficient σ being given by[2]

$$\sigma = \frac{8\pi}{3}\frac{e^4}{m^2c^4}N$$

where e and m are, respectively, the charge and mass of the electron, c is the velocity of light, and N is the number of electrons per unit volume. Knowing N from the experimentally determined value of σ and knowing the number of atoms per unit volume of the scattering material, the number of electrons *per atom* could be computed at once. From the early measurements by Barkla on the magnitude of the scattering coefficient, Thomson[3] computed that the number of electrons per atom was of the order of the atomic weight, taking the atomic weight of oxygen as 16. But from later measurements,[4] Barkla concluded that the number of electrons per atom is, for the lighter atoms at least (except hydrogen), more nearly one-half the atomic weight. The carbon atom, for example, atomic weight 12, has, according to

[1] See THOMSON, J. J.: "The Corpuscular Theory of Matter," Chaps. VI and VII (1907).

[2] Chap. XII, p. 462.

[3] "Electron Theory of Matter," p. 145.

[4] *Phil. Mag.*, vol. 21, p. 648 (1911).

Barkla's measurements, 6 electrons. It was later shown that the scattering coefficient for hydrogen is such as to indicate that it has only 1 electron per atom.

2. A stream of electrons traveling with a very high velocity is able to pass through thin sheets of matter but, in so doing, is diffused, the electrons being deflected, more or less, from their initial direction, as a result of the electrostatic forces acting on the moving electrons when they pass near the electrons in the atoms of the thin sheet. By comparing the computed value of the diffusion with that observed experimentally, Thomson found[1] that the number of electrons per atom should be of the order of the atomic weight, taking the atomic weight of hydrogen as unity.

3. Thomson showed[2] that the dispersion of light by a monatomic gas should be determined by the number of electrons per atom. From data on the dispersion of hydrogen, he concluded that the number of dispersion electrons per atom of hydrogen cannot differ much from unity. Drude found, from similar data on dispersion, that, in general, the number of electrons per unit volume taking part in refraction is somewhat greater than the number of atoms per unit volume, but not much greater, and that the greater the chemical valency of the atom the greater is the number of dispersion electrons per atom. Even in the heavy elements, the number of these "refracting systems" in unit volume was found to be only three or four times the number of atoms. Thomson concluded, however, that it was very probable that, in the heavier atoms, at least, only a small part of the *total* number of electrons in the atom takes part in dispersion and refraction and, therefore, that there are more electrons per atom than data on dispersion alone indicated.

These several lines of evidence did not give an entirely unambiguous answer to the question of the number of electrons per atom, but they indicated, at least, the probable order of magnitude. They made it certain, for example, that the atom of carbon contains not more than a dozen or so electrons. Since the normal atom is electrically neutral, the quantity of *positive* electricity per atom was thus roughly determined. Now, Thomson had shown that the mass of the electron is of the order of one two-thousandth of the mass of the hydrogen atom. It was obvious, therefore, that the total mass of the atom is vastly

[1] "Electron Theory of Matter," p. 151.

[2] *Phil. Mag.*, vol. 11, p. 769 (1906).

greater than the total mass of the comparatively few electrons which it contains; and it was logical to assume that practically the entire mass of the atom is associated with its positive charge.

The problem of atom-model building now became somewhat more definite: (1) The atom contains electrons, the number per atom being of the order of magnitude of, but probably smaller than, the atomic weight. (2) The neutral atom must contain as much positive electricity as there is negative electricity associated with its negative electrons. (3) The mass of the atom is associated with the *positive* charge which it contains. (4) The ensemble of positive charge and negative electrons which make up the atom must be stable; the electrons, for example, must be held by (electrostatic?) forces in fixed positions of equilibrium about which they may vibrate, when disturbed, with the definite frequencies required to explain the characteristic line spectra of the elements. (5) Except when so disturbed, the electrons must be at rest, since, otherwise, they would emit radiation as required by the electromagnetic theory. The much greater mass of the positive charge made it reasonable to assume that it is the *electrons*, rather than the positive charges, which vibrate in the process of emitting radiation.

(*b*) *The Distribution of Positive and Negative Charge in the Atom.*—To meet the requirements of stability and "in default of exact knowledge of the nature of the way in which positive electricity occurs in the atom," Thomson considered "a case in which the positive electricity is distributed in the way most amenable to mathematical calculation, *i.e.*, when it occurs as a sphere of uniform density, *throughout* which the corpuscles[1] are distributed."[2] According to Thomson's proposal, the atom consists of a sphere of radius a, throughout which there is a uniform distribution of positive electricity of density ρ given by

$$\rho = \frac{E}{\frac{4}{3}\pi a^3} \tag{1}$$

where E is the total positive charge contained by the sphere. Stability can be secured by assuming that the electrons are so arranged *inside* the sphere that their mutual repulsions are exactly balanced by the attraction toward the center of the sphere

[1] The modern term is "electrons."

[2] Quotations from THOMSON'S "The Corpuscular Theory of Matter," p. 103.

due to its positive charge. Consider a single electron, charge $-e$, inside the sphere and at a distance r from its center (Fig. 78). Assuming the ordinary laws of electrostatics to apply, it is obvious that the net force exerted on the electron by that part of the positive charge *outside* the sphere of radius r is zero. The total force on the electron is, therefore, due to that part of the positive charge, call it E_r, *inside* the sphere of radius r, and this positive charge acts as if it were concentrated at the center of the sphere. Since, numerically, $E = e$ if the atom is neutral, by use of equation (1) we obtain

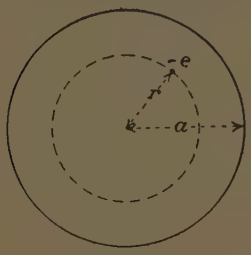

FIG. 78.

$$E_r = e\frac{r^3}{a^3} \tag{2}$$

The force F_c toward the center, acting on the electron, is, therefore,

$$F_c = \frac{eE_r}{r^2} = \frac{e^2}{a^3}r \tag{3}$$

F_c is, of course, zero when r is zero. The position of equilibrium with 1 electron is, therefore, *the center of the sphere*, and the *return force* acting on this electron when displaced should be proportional to r. The vibration should be simple harmonic, and an atom so constituted should be capable of emitting only a single frequency of the order of 10^{15} vibrations per second (taking $e = 4.77 \times 10^{-10}$ e.s.u, $a = 10^{-8}$ cm., and the mass of the electron 9×10^{-28} gram). It is, perhaps, suggestive that the order of magnitude of this frequency corresponds roughly to that observed in spectra. But, of course, no atom is known which omits only a single frequency.

In an atom which contains 2 electrons, the positions of equilibrium are symmetrically situated on opposite sides of the center and are at a distance apart equal to the radius a of the sphere.[1]

[1] This is readily shown to be the case, since, remembering that now $E = 2e$, and calling r the distance of the equilibrium position from the center, the force of attraction F_c on each electron toward the center is

$$F_c = 2e^2\frac{r}{a^3}$$

Three electrons inside the sphere of charge $E = 3e$ are in equilibrium when at the corners of a symmetrically placed equilateral triangle the side of which is equal to the radius a. For 4 electrons, the positions of equilibrium are the corners of a regular tetrahedron the edge of which is equal in length to the radius a.

Continuing in this way, Thomson determined the conditions of equilibrium for larger numbers of electrons. He found, in general, that more than 5 electrons could not exist in stable equilibrium in a single ring, unless there were other electrons *within* the ring. Thus, 6 electrons at the corners of a hexagon are unstable, but stable equilibrium is obtained if 1 of the electrons is put at the center and the remaining 5 at the corners of a regular

FIG. 79.—The Thomson atom model, showing the successive rings of electrons *within* the positive sphere.

pentagon. With 22 electrons, 12 are in an outside ring, 8 in a middle ring, and 2 in an inner ring, as shown diagrammatically in Fig. 79. The way in which the successive rings are formed with the addition of more electrons is suggestive, in a rough, qualitative way, of the repetition of properties of elements in the several columns of the periodic table.

Although now of historical interest only, a table is given[1] by Thomson showing the arrangement of electrons for numbers from 1 to 100 inside the positive sphere. This table is repro-

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and the repulsion F_r, between the electrons is

$$F_r = \frac{e^2}{4r^2}$$

For equilibrium, $F_c = F_r$. The proof that this is a position of *stable* equilibrium is left to the reader.

[1] "The Corpuscular Theory of Matter," p. 109.

duced, in part, in Table I, in order to emphasize the fact that the *prime considerations in Thomson's atom were the requirements of stability, on the one hand, and the demands of the electromagnetic theory, on the other, that the electrons in the normal, neutral atom must be at rest, otherwise they would radiate.*

TABLE I.—ARRANGEMENT OF ELECTRONS IN THE THOMSON ATOM

Total number...	1	2	3	4	5																	
Ring 1.....	1	2	3	4	5																	
Total number...	6	7	8	9	10	11	12	13	14	15	16											
Ring 1[1].....	5	6	7	8	8	8	9	10	10	10	11											
Ring 2.....	1	1	1	1	2	3	3	3	4	5	5											
Total number...	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31							
Ring 1.....	11	11	11	12	12	12	13	13	13	13	13	14	14	15	15							
Ring 2.....	5	6	7	7	8	8	8	8	9	10	10	10	10	10	11							
Ring 3.....	1	1	1	1	1	2	3	3	3	3	4	4	5	5	5							
Total number...	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48					
Ring 1.....	15	15	15	16	16	16	16	16	16	16	17	17	17	17	17	17	17					
Ring 2.....	11	11	11	11	12	12	12	13	13	13	13	13	13	14	14	15	15					
Ring 3.....	5	6	7	7	7	8	8	8	8	9	9	10	10	10	10	10	11					
Ring 4.....	1	1	1	1	1	1	2	2	3	3	3	3	4	4	5	5	5					
Total number...	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	
Ring 1.....	17	18	18	18	18	18	19	19	19	19	20	20	20	20	20	20	20	20	20	21	21	
Ring 2.....	15	15	15	15	16	16	16	16	16	16	16	16	16	17	17	17	17	17	17	17	17	
Ring 3.....	11	11	11	11	11	12	12	12	12	13	13	13	13	13	13	13	14	14	15	15	15	
Ring 4.....	5	5	6	7	7	7	7	8	8	8	8	8	9	9	10	10	10	10	10	10	11	
Ring 5.....	1	1	1	1	1	1	1	1	2	2	2	3	3	3	3	4	4	5	5	5	5	

[1] The rings are numbered starting with the outermost and going inward.

Thomson pointed out that such an arrangement of electrons as is shown in Fig. 79 might, when disturbed, give rise to radiations of many different frequencies, due partly to the vibrations of each electron about its equilibrium position and partly to the orbital revolutions of the rings around the center of the atom. Thomson's model, however, gave no quantitative data on spectra. And, although it conformed to the requirements of stability and the electromagnetic theory, it came ultimately into conflict with the experiments of Rutherford and his collaborators on the scattering of swiftly moving alpha particles, as they pass through thin sheets of matter. These experiments led to a very different atom model—one in which, in order to meet the conditions of stability, *it became necessary, ultimately, to discard the fundamental*

deduction from the electromagnetic theory that an accelerated charge must radiate.

3. The Scattering of Alpha Particles in Passing through Matter.—(*a*) Radioactive materials in the process of decay emit three kinds of rays, or radiations, known, respectively, as the "alpha (α)" the "beta (β)," and the "gamma (γ)" rays. The γ-rays have been shown to be extremely short electromagnetic rays the wave length of which is of the order of 0.001 to 0.1 *A*. The β-rays have been proven to be negatively charged particles with mass and charge identical with the mass and charge of the electron; *i.e.*, the β-rays are electrons ejected from the radioactive atom with very high velocities, approaching, for some kinds of rays, the velocity of light. The α-rays have been shown to be positively charged particles which have (1) a mass exactly equal to that of the helium atom and (2) a positive charge numerically equal to twice the charge on the electron. Since helium is known to result from radioactive decay, the α particles are identified with helium atoms which, since the α particles contain a *twofold* positive charge, have lost 2 electrons. The initial velocity of the α particles, although depending somewhat on the radioactive material from which they originate, is of the order of $2 \cdot 10^9$ cm. per second.

(*b*) These radioactive rays may be studied by means of the various effects which they produce. Among these effects are the flashes of light or scintillations which the particles produce on striking a zinc-sulphide screen, the impact of a *single* particle producing a *single* flash. These flashes are readily observed by a low-power microscope.

If a stream of α particles, limited by means of suitable diaphrams to a narrow cylindrical pencil, be allowed to strike a zinc-sulphide screen placed at right angles to the path of the particles, the scintillations will occur over a well-defined circular area equal to the cross-section of the pencil. If, now, a thin film of matter, such as gold or silver foil, be interposed in the path of the rays, it is found that they pass quite readily through the foil but that the area over which the scintillations occur becomes larger and loses its definite boundary, indicating that some of the particles have been deflected from their original direction. This spreading out of the stream of particles on passing through thin layers of matter, solid or gaseous, is called "scattering."

Qualitatively, it is easy to explain the origin of the forces which cause the deflection of the α particle. The particle itself has a twofold positive charge. The atoms of the scattering material contain charges, both positive and negative. In its passage through the scattering material, the particle experiences electrostatic forces the magnitude and direction of which depend on how near the particle happens to approach to the centers of the atoms past which *or through which* it moves.

If we assume the Thomson model of the atom, with its sphere of positive electrification, inside which are electrons, the path of an α particle in passing *through* such an atom might be as indicated in Fig. 80, the net result of the passage being to deflect the path of the particle through a small angle θ. The major part of this deflection arises from the electrostatic repulsion on the α particle due to the charge on the positive sphere, which, for the heavier atoms at least, has a mass many times that of the α particle. The electrons within the positive sphere, being capable of motion about their respective positions of equilibrium and possessing a mass which is very small compared to the mass of the α particle, will produce no appreciable deflection of the latter. Rather, the electrons themselves would be pulled from their positions of equilibrium and set vibrating by the passage of the α particle. The total deflection of any given particle in passing through or past a number of such atoms in a thin layer of scattering material will be governed by the laws of probability. Thomson showed[1] that the mean deflection ϕ_m of a particle in passing through a thin plate of thickness t should be

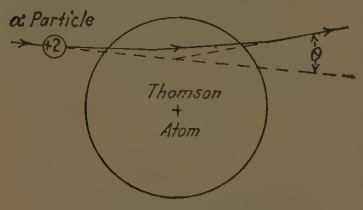


FIG. 80.—The deflection of an α particle in passing through the Thomson atom.

$$\phi_m = \theta\sqrt{N\pi a^2 t} \qquad (4)$$

where θ is the average deflection due to a single atom; N is the number of atoms per unit volume; and a is the radius of the positive sphere.

This process of scattering of the α particles as a result of a large number of small deflections produced by the action of a large number of atoms of the scattering material on a single α

[1] *Proc. Cambridge Phil. Soc.*, vol. 15, p. 465 (1910).

particle is called *multiple*, or *compound*, scattering. It is readily seen that the structure of the atom assumed by Thomson would not result in a large deflection due to any *single* encounter. If, for example, the α particle were to pass through the atom in such a way as to pass near its center (Fig. 81), the forces acting near the center being very small, the resulting deflection would not be large. According to Rutherford,[1] the number of α particles N_ϕ which, as a result of *multiple* scattering, should be scattered through an angle ϕ *or greater* is given by

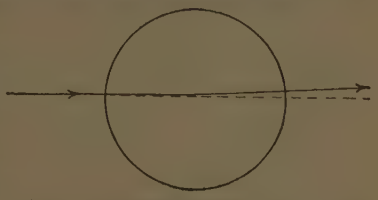


FIG. 81.—The deflection of an α particle which passes very close to the center of a Thomson atom.

$$N_\phi = N_0 e^{-(\phi/\phi_m)^2} \tag{5}$$

where N_0 is the number of particles for $\phi = 0$, and ϕ_m is the average deflection after passing through the scattering material.

(*c*) Now, Geiger had shown[2] experimentally that the most probable angle of deflection of a pencil of α particles in passing through gold foil 1/2,000 mm. thick is of the order of 1 degree. It is evident, therefore, from equation (5), that the probability for scattering through large angles becomes vanishingly small. For 30 degrees, for example, the probability would be of the order of 10^{-13}. Geiger showed that the *observed* scattering obeyed this probability law for *small* angles of scattering but that *the number of particles scattered through large angles was much greater than this theory of multiple scattering predicted.* Indeed, Geiger and Marsden showed[3] that 1 in 8,000 α particles was turned through an angle of *more than* 90 *degrees* by a thin film of platinum, *i.e.*, were, *in effect*, diffusely *reflected.* This so-called "reflection," however, was shown to be not a surface phenomenon but rather a volume effect, since the number of particles turned through more than 90 degrees increased, up to a certain point, with increasing thickness of the scattering foil. It was also found that the proportion of particles diffusely reflected increased approximately as the $\frac{3}{2}$ power of the atomic weight of the foil.

It was impossible to explain this excess scattering of α particles through large angles on the basis of the multiple scattering to be

[1] *Phil. Mag.*, vol. 21, p. 679 (1911).

[2] *Proc. Roy. Soc.*, London, vol. 83, p. 492 (1910).

[3] *Proc. Roy. Soc.*, vol. 82, p. 495 (1909).

expected from the Thomson atom and the laws of probability. There must be something wrong with Thomson's picture of the atom.

4. Rutherford's Nuclear Atom. (*a*) *Rutherford's Hypothesis.* Accordingly, Rutherford, in a classic article[1] which may be regarded as the starting point of our modern ideas on atomic structure, proposed a new type of atom model capable of giving to an α particle a *large* deflection as a result of a *single* encounter. This required that an α particle, to be so deflected, must, at some point in its path past or through an atom, experience much larger forces than the Thomson atom was capable of producing. These large forces could be produced only by assuming *that the*

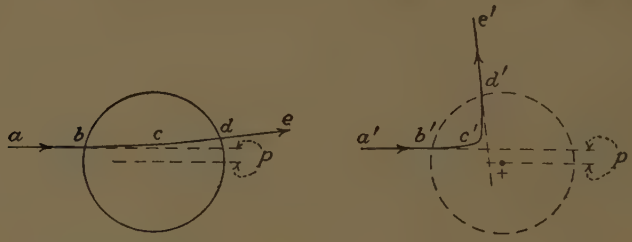


FIG. 82.—Comparison of deflections produced on an α particle by (*a*) the Thomson atom and (*b*) the Rutherford nuclear atom for similar conditions of incidence.

positive charge of the atom, instead of being uniformly distributed throughout a sphere of atomic dimensions, as Thomson had assumed, is concentrated in a very small region less than 10^{-12} *cm. in diameter at the center of the sphere.* This concentrated charge, later called the "nucleus," is (in Rutherford's original article) assumed to be surrounded by a numerically equal *negative* charge distributed, for sake of computation, "uniformly throughout a sphere of radius *R*." This negative charge is, of course, identified with the charge on the electrons which, in Rutherford's atom, *surround* the nucleus in some sort of configuration.

The difference in the effect which the two atoms, Thomson's and Rutherford's, have on an α particle passing in their neighborhood, is shown in Fig. 82. In (*a*) is represented diagrammatically the path of an α particle through Thomson's atom, the initial path of the atom being so directed that, were the particle not

[1] *Phil. Mag.*, vol. 21, p. 669 (1911). Every student of modern physics should read, and thoroughly digest, this article.

deflected, it would pass through the atom at a distance p from its center. As is shown by equation (3), the force which the particle experiences as it penetrates more deeply into the (Thomson) atom becomes less and less. At point c, the force, although at right angles to the path, is a minimum. The deflection produced is small and is equal to the angle between ab and de.

In Rutherford's model (Fig. 82(b)), we have a different state of affairs. Here, an α particle is assumed with an initial path which, were the particle not deflected, would pass the center of the atom at a distance p, the same as in Fig. 82(a). Over the path $a'b'$, the forces which the particle experiences are the same as for the corresponding path in (a). After passing point b', however, the forces continue to *increase* according to the inverse square of the distance between the particle and the nucleus, rather than decrease as was the case in (a). It can be shown, readily, that at a given distance r from the center of the Rutherford atom (r being less than the radius a of the Thomson atom), the force experienced by the α particle is a^3/r^3 times as great as for the corresponding position in the Thomson atom, assuming, in each case, the inverse-square law to hold. The difference in the forces experienced by the α particle in the two cases becomes very great as the particle approaches the center. It is readily seen that the net result of all this is that the Rutherford model gives to the particle a much greater deflection than does the Thomson atom.

Now, the chance that an α particle shall approach the atom along a path which, extended, is distant p from the center is just as great for the Thomson atom as for Rutherford's. But we see that, in the latter case, the deflection is large, as a result of a *single* encounter. In the former case, the deflection is small. It is obvious, therefore, that applying the same laws of probability to the two cases, the proportion of α particles deflected through *large* angles would be much greater for the Rutherford atom than for Thomson's. Rutherford refers to this phenomenon as *single scattering* as distinguished from multiple scattering. It is to be pointed out that multiple scattering is still present, of course, with the Rutherford model but becomes of importance only for very small angles of scattering.

The scattering is usually measured by allowing the particles after passing through the foil F (Fig. 83) to fall on the zinc-sulphide screen S placed normal to the initial path of the par-

ticles. By means of a low-power microscope, the number of particles per unit area striking the screen in the neighborhood of P is observed for various angles of scattering ϕ. Rutherford, in the article referred to, shows that on the basis of the nuclear type of atom the number of particles per unit area striking the screen should be proportional to

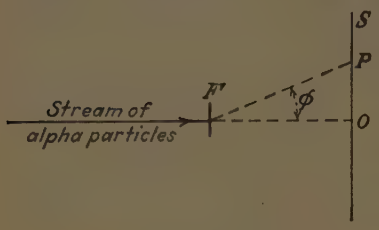


FIG. 83.

(1) $1/\sin^4\frac{\phi}{2}$;

(2) the thickness t of the scattering material, for *small* values of t;

(3) $(Ze)^2$ where e is the charge on the electron and Z is a multiple depending on the atom;

(4) inversely proportional to the square of the initial kinetic energy of the particles.

(*b*) *Experimental Confirmation.*—These predictions were completely verified by the experiments of Geiger and Marsden.[1] Table II, taken from their paper, shows the number of scintillations observed per unit area on the zinc-sulphide screen, for the various angles of scattering, for gold and for silver foils. The data

TABLE II.—ANGULAR DISTRIBUTION OF SCATTERED α PARTICLES[1]

Angle, degrees	$\frac{1}{\sin^4\frac{\phi}{2}}$	Number of scintillations per unit area	
		Silver	Gold
150	1.15	22.2	33.1
135	1.38	27.4	43.0
120	1.79	33.0	51.9
105	2.53	47.3	69.5
75	7.25	136	211
60	16.0	320	477
45	46.6	989	1,435
37.5	93.7	1,760	3,300
30	223	5,260	7,800
22.5	690	20,300	27,300
15	3,445	105,400	132,000

[1] From GEIGER and MARSDEN: *Phil. Mag.*, vol. 25, p. 610 (1913).

[1] *Phil. Mag.*, vol. 25, p. 605 (1913).

are shown graphically in Fig. 84, in which the logarithms of the number of scintillations per unit area are plotted as abscissæ against the logarithms of $1/\sin^4 \frac{\phi}{2}$

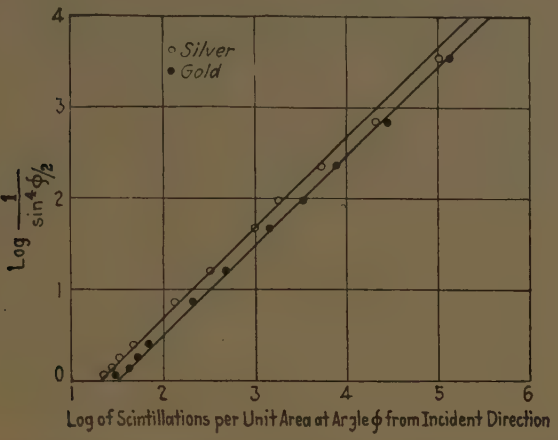


FIG. 84.—The law of the scattering of α particles: ϕ is the angle of scattering.

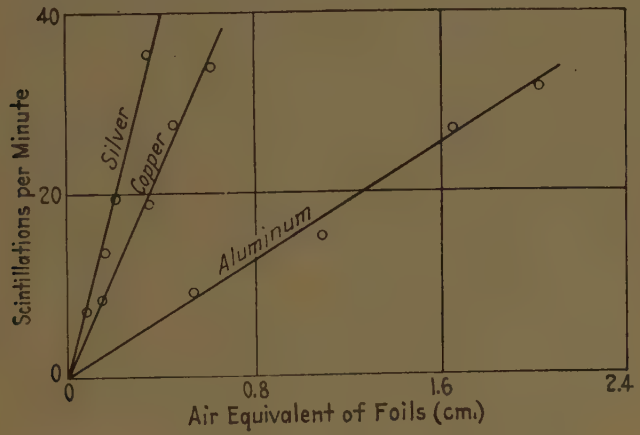


FIG. 85.—Showing that at a given angle of scattering, the number of scattered particles per unit area is proportional to the thickness of the scatterer.

as ordinates. If these two quantities are proportional to each other, the points, for each substance, should lie on a straight line inclined at 45 degrees with the axes. The two lines are

drawn at *exactly* 45 degrees with the axes, and the observed points are seen to agree well with the predictions. This is the more remarkable since, as the table shows, the number of scintillations per unit area cover a very wide range of values.

In Fig. 85 (taken from the paper by Geiger and Marsden) is shown the number of scintillations per minute as a function of the thickness of the scattering material for several different metals. The prediction of Rutherford that the scattering should, for small thicknesses, be proportional to thickness is seen to be confirmed. It will be recalled (see equation (4)) that, on the theory of multiple scattering by the Thomson atom, the *square root* of the thickness is involved. The decision is, therefore, quite emphatically in favor of the nuclear type of atom.

Geiger and Marsden also showed, in confirmation of the fourth of Rutherford's predictions, that "the amount of scattering by a given foil is approximately proportional to the inverse fourth power of the velocity (inverse square of the energy) of the incident α particles," over a range of velocities such that the number of scattered particles varied as 1:10.

(*c*) *Atomic Number.*—Geiger and Marsden further concluded, from a study of the variation of scattering with atomic weight and of the fraction of the total number of incident particles scattered through a given angle, (1) that the scattering is approximately proportional to the atomic weight of the scatterer over the range of elements from carbon to gold and (2)[1] that "*the number of elementary charges composing the center of the atoms is equal to half the atomic weight.*" This second conclusion was in agreement with Barkla's experiments on the scattering of X-rays previously mentioned (p. 331), which determined the number of *electrons* associated with an atom. According to these results, carbon, nitrogen, and oxygen should have, respectively, 6, 7, and 8 electrons. Now, these elements are, respectively, the sixth, seventh, and eighth elements in the periodic table. The hypothesis was natural, therefore, that *the number of electrons in the atom is numerically equal to the ordinal number which the atom occupies in the series of the elements, counting hydrogen as the first.* This assumption gives to hydrogen 1 electron, in agreement with the data on the scattering of X-rays by hydrogen. Helium would then have 2 electrons and a twofold positive charge on the nucleus; and we see, therefore, that the α particles, which have

[1] For details see the original paper.

been shown to be helium atoms with a twofold positive charge, are helium nuclei. Lithium, the third element, should have 3 electrons and a threefold positive charge on the nucleus. Neon, the tenth element, should have 10 electrons; and so on. Thus originated the concept of *atomic number*, the importance of which, in determining atomic properties, was soon to be emphasized by the pioneer work of Mosley in the X-ray spectra of the elements. The *atomic number*, symbol Z, of an element we may think of variously as (1) the ordinal number of the element in the series of the elements starting with $Z = 1$ for hydrogen; or (2) the (net)[1] positive charge carried by the nucleus of the atom, in terms of the electronic charge e as a unit; or (3) the number of electrons surrounding the nucleus in the normal, neutral atom.

These experiments of Geiger and Marsden so completely confirmed the conclusions which Rutherford had reached by

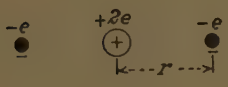


FIG. 86.

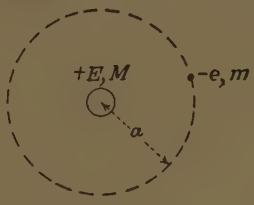


FIG. 87.

postulating the nuclear type of atom that, in spite of very weighty objections, the Rutherford atom model was, at once, universally adopted.

(*d*) *Some Difficulties.*—The objections to the nuclear type of atom, in which the positive charge occupies a negligibly small volume at the center of the atom and is surrounded by negatively charged electrons in sufficient number to make the atom electrically neutral, are, in large part, concerned with questions of stability, which conditions formed the very foundation on which the Thomson model was built. It is obvious that, in the Rutherford atom model, equilibrium cannot be secured, if the electrons are at rest, by the operation of electrostatic forces alone. For, consider (Fig. 86) a nucleus with a double positive charge $+2e$ and with 2 electrons symmetrically placed at a distance r from the nucleus. Assuming the inverse-square law, the attraction of the nucleus for each electron is $2e^2/r^2$, while the electrons repel

[1] We shall see, later (Chap. XIII), why we say "net" charge.

each other with a force equal to only one eighth of this, namely, $e^2/(2r)^2$. The electrons will, therefore, "fall into" the nucleus.

Nothing is gained by giving to the electron an orbital motion, as that of the earth round the sun. Let the nucleus (Fig. 87) have a charge $+E$ and a mass M. Let a single electron, charge $-e$, mass m very small compared to M, revolve around the nucleus in a circular orbit of radius a at such velocity v that

$$\frac{Ee}{r^2} = \frac{mv^2}{r} \tag{6}$$

We should then have *mechanical* equilibrium, the centripetal force being balanced by the electrostatic attraction. But according to the fundamental laws of the electromagnetic theory, such a revolving electron, since it is subject to a constant acceleration toward the center of its orbit, should radiate energy. This energy can come only from the energy, part potential, part kinetic, of the system. The system will, therefore, "run down" the electron approaching the nucleus by a spiral path *and giving out a radiation of constantly increasing frequency.* This, however, is contrary to observation. From the standpoint of stability, the Thomson model is much to be preferred. Yet the experiments of Geiger and Marsden and their interpretation by Rutherford on the basis of the nuclear model of the atom were not to be denied. It was at this point that Bohr introduced his epoch-making theory of the structure of the atom and of the origin of spectra.

5. The Phase Integral.—Bohr's celebrated theory of atomic structure is, in effect, an extension of Planck's theory of quanta applied to Rutherford's nuclear atom in an attempt, extraordinarily successful, to explain the origin of the characteristic spectra of the elements. It is indicative of something very fundamental to both temperature radiation and characteristic spectra that, although these two types of radiation differ from each other in important respects—since the former depends only on the temperature of the source and is quite independent of the kind of matter acting as emittor, while the frequency of the latter depends *only* on the kind of atom and is quite independent of the temperature—the same revolutionary concepts of quanta should be successfully applied to both, classical methods having in each case failed.

Let us return, for a moment, to Planck's linear oscillator, discussed in Chap. VIII, and let us, for simplicity, think of it as

having only mechanical properties; the fundamental principles involved are not changed thereby. In Fig. 88, let a particle of mass m vibrate with simple harmonic (linear) motion about a

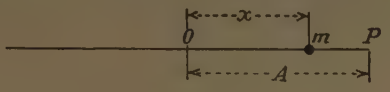


FIG. 88.

center O with an amplitude A and a frequency ν. The displacement x at any instant is given by

$$x = A \sin 2\pi\nu t \tag{7}$$

where t is the time measured from an instant when the particle is at the center O. The energy W of the system oscillates between all kinetic at O and all potential at maximum displacement. Planck's assumption was that the oscillator could have energy only in multiples of $h\nu$, *i.e.*, that

$$W = \tau \cdot h\nu \tag{8}$$

where τ is an integer and h is Planck's constant, the numerical value of which is 6.55×10^{-27} erg. sec.

The total energy of the system is obtained by computing the kinetic energy $W = \frac{1}{2}mv^2_{max}$ at midposition. Since

$$\left.\begin{aligned} v &= \frac{dx}{dt} = 2\pi\nu A \cos 2\pi\nu t \\ \text{and} \\ v_{max} &= 2\pi\nu A \end{aligned}\right\} \tag{9}$$

$$\therefore W = \tfrac{1}{2}mv^2_{max} = 2\pi^2\nu^2A^2m \tag{10}$$

As the particle oscillates, its *momentum* p_x changes from zero at maximum displacement P to a maximum at midpoint O. The momentum at any point in the path is given by

$$p_x = m\frac{dx}{dt} = 2\pi\nu Am \cos 2\pi\nu t \tag{11}$$

Now, plot a curve (Fig. 89) with p_x as ordinates and the displacement x as abscissæ. The figure can readily be shown to be an ellipse. (The proof of this is left to the student.) The area S of the figure is obviously given by

$$S = \int p_x dx \tag{12}$$

taken over the complete cycle. Since

$$dx = 2\pi\nu A(\cos 2\pi\nu t)dt \tag{13}$$

we have, using equations (11) and (12),

$$S = 4\pi^2\nu^2 mA^2 \int_{t=0}^{t=1/\nu} (\cos^2 2\pi\nu t)dt \tag{14}$$

$$\therefore S = 2\pi^2\nu mA^2 * \tag{15}$$

If we write equation (15) in the form

$$S = \frac{2\pi^2\nu^2 mA^2}{\nu} \tag{16}$$

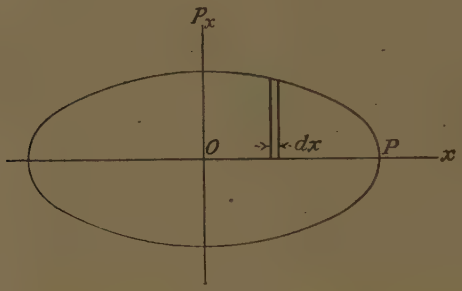


FIG. 89.

the numerator, according to equation (10), is equal to W, the energy of the system; and, by equation (8), $W = \tau \cdot h\nu$. Equation (16), therefore, becomes, using the right-hand side of equation (12) for S,

$$\oint p_x dx = \frac{\tau \cdot h\nu}{\nu} = \tau \cdot h \tag{17}$$

where $\oint$ means "integration over a complete cycle."

That is to say: *On the basis of Planck's hypothesis, as given by equation* (8), *the integral* $\int p_x dx$, *taken over a complete cycle, can take on only a series of values obtained by multiplying the universal constant h by the integers* 0, 1, 2, 3 . . . In terms of Fig. 89, this means that out of the infinite number of ellipses *geometrically* possible, we have a limited number: one ellipse for $\tau = 1$, another for $\tau = 2$, another for $\tau = 3$, etc. The area *between* successive ellipses is numerically equal to h.

* $\int_0^{1/\nu} (\cos^2 2\pi\nu t)dt = \frac{1}{2\nu}$.

This integral in equation (17) is spoken of as the *phase integral.* Its value is derived here for the case of an harmonic oscillator to which Planck's quantum conditions are assumed to apply. We may assume, however, in accordance with the heuristic methods of applying the quantum conditions, that an equation of the type of equation (17) is generally applicable wherever with any coordinate q (corresponding to x) there is associated a momentum p (corresponding to p_x). So that, in general, we may apply to the coordinate q and the corresponding momentum p the integral

$$\oint p dq = \tau h \tag{18}$$

To illustrate, let us apply this equation (18) to the case of a body moving in uniform circular motion, as, for example (since we shall consider this case a little later), the motion of an electron around a nucleus (Fig. 90) in the Rutherford type of atom, disregarding for the moment electromagnetic radiation. The coordinate in terms of which the motion is described is an angle ϕ measured from some arbitrary starting point. Corresponding to this (angular) coordinate ϕ is the *angular* momentum p_ϕ of the electron around the nucleus, p_ϕ being equal to the product of the *moment of inertia* of the electron taken about O by the *angular velocity* about the same point. As applied to this case, equation (18) may be written,

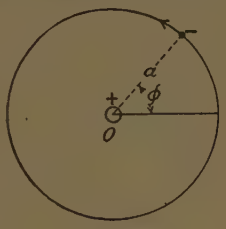


FIG. 90.

$$\oint p_\phi d\phi = \tau h \tag{19}$$

The angular velocity being assumed constant, p_ϕ is constant, and, since $\oint d\phi = 2\pi$, we have

$$2\pi p_\phi = \tau h$$

or

$$p_\phi = \tau \frac{h}{2\pi} \tag{20}$$

This is an important equation to which we shall refer presently. It states that, under the restrictions of Planck's quantum conditions, the *angular* momentum p_ϕ of an electron moving in a cir-

cular orbit around a (massive) positively charged nucleus may take on only those values which are integer multiples (τ) of $h/2\pi$. It should be emphasized that this equation follows, more or less logically, from Planck's quantum hypothesis $W = \tau \cdot h\nu$.

We shall now return to Bohr's development.

6. Bohr's Extension of the Nuclear Atom Model.—(*a*) We are now in position (1) to apply to the Rutherford atom model the principle, derived in the preceding section (equation (20)), that the angular momentum of an electron in orbital (circular)[1] motion around a nucleus may take on only a series of discrete values given by $\tau \frac{h}{2\pi}$ and (2) by aid of two new postulates introduced by Bohr, to derive an equation for the Balmer's series of lines in the spectrum of hydrogen.

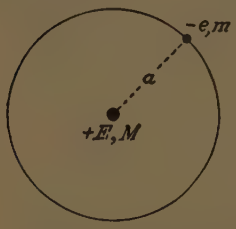


FIG. 91.—The Bohr atom model for a nucleus with a single electron.

Let Fig. 91 represent a nuclear atom with a nucleus of charge $+E$ and mass M around which moves in a circular orbit a single electron of charge $-e$ and mass m, the radius of the orbit being a. M is so large compared to m that, for the present, we shall assume the nucleus to remain at rest. Assuming the inverse-square law of electrostatic attraction to apply, the system will be in equilibrium, according to the ordinary laws of *mechanics*, when

$$\frac{Ee}{a^2} = \frac{mv^2}{a} \tag{21}$$

where v is the linear velocity of the electron in its orbit. This equation at once becomes

$$\frac{Ee}{2a} = \frac{1}{2}mv^2 = T, \tag{22}$$

T being the kinetic energy[2] of the electron. Now, the potential V at a distance a from the (point) charge $+E$ is, assuming the zero of potential to be at an infinite distance from E,

$$V = \frac{E}{a} \tag{23}$$

[1] The path of an electron around a massive central nucleus is, in general, an ellipse, to which Kepler's laws of planetary motion apply. The circular orbit is a special case. We shall discuss the more general case later.

[2] We assume, for simplicity, that m does not vary with velocity (see Sec. 8, *infra*).

and the *potential energy* U of the system when a charge $-e$ is at the distance a from E is

$$U = -e\frac{E}{a} \tag{24}$$

The total energy W of the system is equal to the sum of the kinetic and the potential energy. Therefore,

$$W = T + U = \frac{Ee}{2a} - \frac{Ee}{a} = -\frac{Ee}{2a} \tag{25}$$

A comment, at this point, regarding equations (22) and (24) may be instructive. An electron, coming from infinity to a distance a from the charge E "does" work in amount Ee/a, according to equation (24). Of this work, only one half, namely, $Ee/2a$, by equation (22), remains in the system as kinetic energy. What has become of the other half? The answer, on the classical theory, is obvious: In coming from infinity to the orbit in question, *by whatever path*, the electron has experienced acceleration, as a result of which it must have radiated. Without a knowledge of the acceleration experienced at each point in the path, we cannot compute the amount of energy so radiated. But we may apply the law of the conservation of energy and conclude with confidence that the missing energy has been radiated. If the path from infinity to the orbit of radius a has been a spiral, the frequencies in this radiated energy would range from zero to $\omega/2\pi$ where ω is the angular velocity in the orbit of radius a.

(*b*) On the classical theory, this circular orbit of radius a could not be a permanent orbit. It should be, rather, a part of the spiral path by which the electron reaches the nucleus. Consequently, a could assume *any value whatever*. But now Bohr introduces his first hypothesis:

> *that the values of the angular momentum and, therefore, of the radius a are restricted to certain discrete values* (as required by equation (20)) *and that, therefore, only a limited number of orbits are possible; further, that* ***these orbits are stable orbits and that the motion of the electron in them is governed by the ordinary laws of mechanics, and electrostatics, but is not subject to the requirements of the electromagnetic theory.*** In other words, Bohr assumes that, *while moving in these orbits, the electron does not radiate.*

How are these privileged orbits chosen; what are the various possible values of the radius a? This question is answered at once by introducing the equation (20)

$$p_\phi = \tau \frac{h}{2\pi} \tag{20}$$

Since $p_\phi = ma^2 \cdot \omega$ (*i.e*, moment of inertia times angular velocity), we have the equation

$$ma^2\omega = \tau \frac{h}{2\pi} \tag{26}$$

Introducing $v = \omega a$ into equation (22), we have

$$\frac{1}{2} m(\omega a)^2 = \frac{Ee}{2a} \tag{27}$$

Eliminating ω between equations (26) and (27) and solving for a, we have

$$a = \tau^2 \cdot \frac{h^2}{4\pi^2 mEe} \tag{28}$$

That is, *the radii a of the successive privileged orbits are proportional to the squares of the integers* 1, 2, 3 . . . These integers are called the *quantum numbers* of the respective orbits. Applying equation (28) to the hydrogen atom for which $E = e = 4.774 \times 10^{-10}$ e.s.u., and taking $m = 9 \times 10^{-28}$ gm. and $h = 6\ 55 \times 10^{-27}$ erg. sec., we find that the successive radii a_H of the permissible orbits around the hydrogen nucleus are given by

$$a_H = \tau^2 \cdot 0.53 \times 10^{-8} \text{ cm.}$$

Since τ cannot be less than unity, the radius of the *smallest possible orbit* in the hydrogen atom is 0.53×10^{-8} cm.; or the diameter of the orbit is of the order of 10^{-8} cm., *which is exactly the order of magnitude of the diameters of atoms computed from the kinetic theory of gases.* The diameters of the other orbits will be, approximately, 4×10^{-8}, 9×10^{-8}, 16×10^{-8}, etc. Corresponding to each of these orbits, the system has a definite amount of energy W which is at once obtained by putting into equation (25)

$$W = -\frac{Ee}{2a} \tag{25}$$

the value of a from equation (28). This gives

$$W_\tau = -\frac{2\pi^2 mE^2e^2}{\tau^2 h^2} \tag{29}$$

where W_τ stands for the energy of the system when the electron is in the τth orbit. We see that the larger the value of τ the *smaller numerically* but the *larger in absolute value* (because of the minus sign) is the energy of the system. For hydrogen, the value of W_τ for the first orbit, taking the values of m, e, and h as before, is -2.15×10^{-11} ergs; for the second, -0.535×10^{-11} ergs; for the third, -0.238×10^{-11} ergs; and so on. The lowest value of W_τ is that corresponding to the *first* orbit. Accordingly, this orbit should be *the most stable and is the one which the electron finally occupies in the normal hydrogen atom.*

(*c*) *If we grant the quantum postulates*, however much they may conflict with the older classical ideas, we see that the problem of *stability* in the nuclear atom is now solved, *but at the expense of throwing away the only picture which we had of the mechanism by means of which the atom could radiate energy:* for we now assert that an electron in revolution in one of the privileged orbits *does not obey the electromagnetic laws;* and Bohr's postulates provide no picture of the sequence of events during transitions *between* orbits.

It is an experimental fact, however, that atoms radiate. We have seen (equation (29)) that the larger the quantum number τ of a given orbit (and, therefore, by equation (28), the larger its radius) *the greater is the energy W_τ of the system.* If, now, an electron, initially revolving in an outer orbit of quantum number τ_2, "drops," as a result of some kind of atomic catastrophy, to an inner orbit of quantum number τ_1, *energy, in amount W_R given by* (remember that $\tau_2 > \tau_1$)

$$W_R = W_{\tau_2} - W_{\tau_1} \tag{30}$$

has disappeared somewhere. By analogy with the classical picture and again placing implicit confidence in the law of the conservation of energy, we may *guess* that this energy W_R *has been radiated.* How? That question we cannot answer. Let us take the guess as similar to an axiom based on observation, just as was Newton's inverse-square law of gravitational attraction or Faraday's laws of electromagnetic induction, neither of which could be explained in terms of more fundamental concepts.

Now, equation (30) is so similar to equation (24), Chap. IX, namely,

$$h\nu = W_1 - W_2 \quad \cdots \quad \text{[(24), Chap. IX]}$$

—which latter equation, be it remembered, was set up *by introducing Planck's quantum postulate into the empirical data on spectral series*—that Bohr was led to his second postulate, namely,

> *that, when an electron drops from an outer to an inner orbit, an amount of energy W_R equal to the difference $(W_{\tau_2} - W_{\tau_1})$ between the energy in the respective orbits is radiated as a quantum of energy of frequency ν given by the equation*
>
> $$h\nu = W_{\tau_2} - W_{\tau_1} \qquad (31)$$

(*d*) The quantities W_{τ_2} and W_{τ_1} now give us an interpretation of the *terms* of the formulæ for spectral series discussed in Chap. IX: Interpreted as in equation (24) of that chapter, these terms are simply the amounts of energy possessed by the atom in its various *stationary states*, using the expression "stationary state" to mean the condition or state of the atom when its electrons are revolving in their several *privileged*, or *stationary*, orbits.

We are thus led at once to a formula for spectral series by putting into equation (31) the respective values of W_τ given by equation (29), *viz.*,

$$W_{\tau_1} = -\frac{2\pi^2 mE^2e^2}{h^2} \cdot \frac{1}{\tau_1^2}$$

$$W_{\tau_2} = -\frac{2\pi^2 mE^2e^2}{h^2} \cdot \frac{1}{\tau_2^2}$$

and we have

$$h\nu = W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 mE^2e^2}{h^2}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \qquad (32)$$

$$\therefore \nu = \frac{2\pi^2 mE^2e^2}{h^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \qquad (33)$$

Or, in terms of wave number n, instead of frequency ν,

$$n = \frac{2\pi^2 mE^2e^2}{ch^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \qquad (33')$$

This equation suggests a very simple picture of the origin of spectral lines: A spectral line originates when an electron initially in revolution in an outer orbit of quantum number τ_2 "drops" to an inner orbit of quantum number τ_1, the frequency of the line being given by equation (33). A whole *series* of lines corresponds to the dropping of electrons from *various* outer orbits (*i.e.*, various

values of τ_2) into a *given* inner orbit, designated by τ_1. Indeed, *equation* (33) *is identical in form with the empirical formula for the Balmer's series of lines in the spectrum of hydrogen* (equation (27), Chap. IX), *viz.*,

$$n = N_H\left(\frac{1}{a^2} - \frac{1}{m^2}\right) \qquad [(27), \text{Chap. IX}]$$

in which[1] $a = 2$ and $m = 3, 4, 5 \cdots$

Remembering that for hydrogen $E = e$, we have *Bohr's formula for the hydrogen spectrum:*

$$n = \frac{2\pi^2 me^4}{ch^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \qquad (34)$$

These formulæ (equation (27), Chap. IX, and equation (34)) *are identical* by setting:

$$\tau_1 = a = 2$$
$$\tau_2 = m = 3, 4, 5, \cdots$$
$$N_H = \frac{2\pi^2 me^4}{ch^3} \qquad (35)$$

A crucial test of equation (34) is the value which equation (35) predicts for the Rydberg constant N_H. Putting into equation (35) the values[2] of m, e, c, and h, we have

$$N_H = \frac{2\pi^2 \times 9.00 \cdot 10^{-28} \times (4.774 \cdot 10^{-10})^2}{2.998 \cdot 10^{10} \times (6.554 \cdot 10^{-27})^3} = 109{,}300$$

which differs by only a fraction of 1 *per cent from the value of* N_H, 109,679, *quoted on page* 303. Bohr's theory, therefore, not only leads to an expression (equation (34)) for the Balmer's series in hydrogen, which is of the same *form* as that found empirically, but also, what is quite astonishing, *it actually predicts the numerical values of the frequencies of the lines almost within the limits of experimental error involved in the determinations of the constants m, e, c, and h!*

(*e*) A picture, based on the quantum theory, of the origin of the *Balmer's series* of lines in hydrogen is, thus, reasonably complete. The various lines originate when electrons fall from outside orbits, the quantum numbers of which are given by the various values of τ_2, into the second orbit of the hydrogen atom,

[1] We shall now use N_H, instead of N_∞, as the Rydberg constant for *hydrogen.*

[2] Taken from the International Critical Tables.

i.e., the one for which $\tau_1 = 2$. Thus, the first line H_α of the series is produced when an electron falls from the third orbit ($\tau_2 = 3$) to the second orbit ($\tau_1 = 2$); the second line H_β, by a transition from the fourth orbit ($\tau_2 = 4$) to the second orbit; and so on. Of course, a given atom can, at a particular instant, emit only 1 frequency, namely that corresponding to the particular transition which it is experiencing at that instant. In the actual production of the hydrogen, or any other, spectrum in the laboratory, a very large number of atoms participate. In some atoms, transitions giving rise to H_α occur. In others, H_β, H_γ, H_δ . . . are pro-

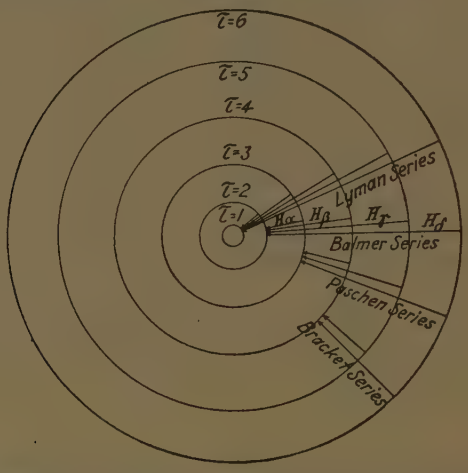


FIG. 92.—"Privileged" circular orbits surrounding the hydrogen nucleus, showing the interorbital transitions which give rise to the various lines in the hydrogen spectrum.

duced. The number of atoms involved is so large and there are so many transitions of a given kind occurring each second, that, to an observer, the lines *appear* to be produced continuously and to be of constant relative intensity. If we could observe the spectrum of hydrogen as produced by only a few hundred atoms, the lines would appear in flashes, first one line, then another, the relative frequency of the flashes in the several lines being proportional to their relative intensities as actually observed.

7. Further Successes of the Rutherford-Bohr Atom Model. (*a*) *Other Series in the Spectrum of Hydrogen.*—The Balmer series of lines in hydrogen is represented diagrammatically in Fig. 92, by the transitions of electrons between orbits $3 \rightarrow 2$, $4 \rightarrow 2$, $5 \rightarrow 2$ · · · · It is obvious that one may, also, expect transitions

between outer orbits and orbit number 1 and also between outer orbits and orbit number 3. The first of these two groups of transitions should give rise to the series of lines given by the formula

$$n = N_{\mathrm{H}}\left(\frac{1}{1^2} - \frac{1}{\tau_2^2}\right)$$

where $\tau_2 = 2, 3, 4 \cdots$ This series, as computation from the known value of N_{H} readily shows, should lie in the ultra-violet. Actually, such a series of lines, known as the "Lyman series," was found by Lyman in the ultra-violet. Four of these lines are shown in Table III. The orbital transitions giving rise to their origin are represented diagrammatically in Fig. 92.

TABLE III.—THE LYMAN SERIES IN THE SPECTRUM OF HYDROGEN:

$$n = N_{\mathrm{H}}\left(\frac{1}{1^2} - \frac{1}{\tau_2^2}\right), \ \tau_2 = 2, 3, 4, \cdots$$

τ_2	λ Ångströms	n
2	1,216.0	82,260
3	1,026.0	97,480
4	972.7	102,820
5	949.7[1]	105,300
∞	.....	109,678

[1] LYMAN: *Nature*, vol. 118, p. 156 (1926).

Transitions to the third orbit should give rise to a series in the infra-red. Several lines of such a series, called the "Paschen series," are known. They are shown in Table IV.

TABLE IV.—THE PASCHEN SERIES IN THE SPECTRUM OF HYDROGEN:

$$n = N_{\mathrm{H}}\left(\frac{1}{3^2} - \frac{1}{\tau_2^2}\right), \ \tau_2 = 4, 5, 6, \cdots$$

τ_2	λ Ångströms	n
4	18,756[1]	5,331.5
5	12,821[1]	7,799.7
6	10,900[2]	9,180
7	10,100[2]	9,090
8	9,500[2]	10,500
∞	.....	12,186

[1] Observed by Paschen.
[2] Observed by Brackett, *Nature*, vol. 109, p. 209 (1922).

Brackett has also observed two lines in the far infra-red spectrum of hydrogen which correspond to transitions from the fifth and the sixth orbits, respectively, to the fourth. These are given in Table V.

TABLE V.—THE BRACKETT SERIES IN THE SPECTRUM OF HYDROGEN: $n = N_H\left(\frac{1}{4^2} - \frac{1}{\tau_2^2}\right)$, $\tau_2 = 5, 6, \cdots$

τ_2	λ (cm.)	n
5	4.05×10^{-4}	2470
6	2.63	3800
∞	.....	6855

With these several series of lines as actually observed in the laboratory, the Bohr theory is in excellent agreement, not only qualitatively *but also quantitatively.*

(*b*) *The Spectrum of Helium.*—Mention was made in Chap. IX (p. 319) of three series of lines in the *spark* spectrum of helium given by the equation (29), Chap. IX:

$$n = 4N_{He}\left(\frac{1}{a^2} - \frac{1}{m^2}\right) \qquad [(29), \text{Chap. IX}]$$

where for each series a takes on the respective values 2, 3, or 4, and m has corresponding values 3, 4, 5 . . . ; 4, 5, 6 . . . ; 5, 6, 7 . . . These *spark* lines occur when the conditions of excitation are very intense.

Equation (33′)

$$n = \frac{2\pi^2 mE^2e^2}{ch^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \qquad (33')$$

gives the general series formula for a nucleus of charge $+E$ around which revolves a *single* electron. (*The formula does not apply to more complicated systems.*) Now, helium, the second element in the periodic table, has a nucleus with a twofold positive charge $E = 2e$ and, normally, 2 electrons. With intense excitation, however, it may be supposed that, occasionally, both these electrons are removed and the bare helium nucleus remains. This nucleus, with its twofold positive charge, should then behave, in "capturing" an electron, in much the same way as the hydrogen nucleus. Equation (33′) should, accordingly,

predict the resulting spectral series in helium, if we put $E = 2e$. We should, therefore, expect series of lines in the spark spectrum of helium the wave numbers n_{He} of which are given by

$$n_{He} = 4 \cdot \frac{2\pi^2 me^4}{ch^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \qquad (36)$$

where τ_1 and τ_2 take on appropriate values. The constant multiplying the bracket is seen to be $4N_H$ if we set N_H equal to $2\pi^2 me^4/ch^3$, according to equation (35). Equation (36) is *very nearly* in agreement with the empirical equation (29), Chap. IX, for the several series in the spark spectrum of helium, given on page 319. There is, however, a slight numerical discrepancy, which becomes significant when measurements of spectroscopic precision are considered; if we determine the Rydberg constant N_H from the *hydrogen* spectrum, we find (see p. 303)

$$N_H = 109{,}679.2$$

The experimental value of $4 \cdot N_{He}$ in equation (29), Chap. IX (see page 319) gives for N_{He},

$$N_{He} = 109{,}723.22$$

(*c*) *The Spectroscopic Value of the Ratio of the Mass of the Electron to That of the Hydrogen Atom.*—This slight discrepancy, mentioned in the preceding paragraph, in the two values of the Rydberg constant, as determined from hydrogen and from the spark spectrum of helium, although they differ by only a few parts in 10,000, has led to a very important deduction from, and, incidentally, to a very surprising confirmation of, the Bohr theory. In setting up the fundamental equations (21) and (22)

$$\frac{Ee}{a^2} = \frac{mv^2}{a} \qquad (21)$$

$$\frac{Ee}{2a} = \frac{1}{2}mv^2 = T \qquad (22)$$

as the starting point of Bohr's theory, we assumed that the mass M of the nucleus is so large in comparison with the mass m of the electron that the nucleus remains at rest with respect to (and, of course *at*) the center around which the electron revolves. Strictly speaking, this is not true; for both masses revolve about

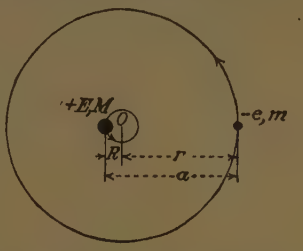


FIG. 93.—The revolution of the nucleus and the electron of the Bohr atom about their common center of gravity.

their common center of gravity O, the nucleus in a small circle of radius R (Fig. 93) and the electron in a larger circle of radius r. As before (p. 350), letting a represent the distance between nucleus and electron, we have, from ordinary mechanics, the relations

$$R = a\frac{m}{M+m} \tag{37a}$$

$$r = a\frac{M}{M+m} \tag{37b}$$

We must now write, instead of the single equation (21), two equations, *viz.*,

$$\frac{Ee}{a^2} = \frac{MV^2}{R} \tag{38a}$$

$$\frac{Ee}{a^2} = \frac{mv^2}{r} \tag{38b}$$

where $V = \omega R$ is the velocity of the nucleus and $v = \omega r$ is the velocity of the electron, ω being the common angular velocity of the system about its center of gravity. The total kinetic energy T of the system is now made up of two parts: that of the nucleus T_M and that of the electron T_m. Introducing the values of R and r from equations (37), we may, analogously with equation (22), change equations (38) to

$$\frac{Ee}{2a}\cdot\frac{m}{M+m} = \frac{1}{2}M(\omega a)^2\left(\frac{m}{M+m}\right)^2 = T_M \tag{39a}$$

$$\frac{Ee}{2a}\cdot\frac{M}{M+m} = \frac{1}{2}m(\omega a)^2\left(\frac{M}{M+m}\right)^2 = T_m \tag{39b}$$

Since the total kinetic energy T of the system is

$$T = T_M + T_m$$

we have, by adding equations (39),

$$T = \frac{Ee}{2a} = \frac{1}{2}\left[m\frac{M}{M+m}\right](\omega a)^2 \tag{40}$$

We thus obtain the same value, namely $Ee/2a$, for the total kinetic energy of the system as when we considered M infinite (equation (22)).

To compare equation (40) with the corresponding equation (22), we may write the latter

$$T = \tfrac{1}{2}m(\omega a)^2 \tag{23'}$$

We may think of these two expressions for T, namely, equations (23′) and (40) as differing from each other only in the fact that in equation (40) the mass m of the electron is multiplied by the factor $M/(M + m)$. Without following through the entire deduction, we can proceed to the final result simply by replacing m in equation (33′) for the spectral series by $m \cdot M/(M + m)$. We then have for the general equation of a spectral series in the nuclear type of atom, in which the mass of the nucleus is *not* (taken as) infinite with respect to the mass of the electron,

$$n = \frac{2\pi^2 mE^2e^2}{ch^3} \cdot \frac{M}{M + m}\left[\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right] \tag{41}$$

We now see that the factor multiplying the bracket, which factor contains the Rydberg constant, *depends on the ratio of the mass of the electron to that of the nucleus.* This gives a clue to the observed difference in the values of the Rydberg constant as computed from hydrogen and from ionized helium.

For, letting M_H and M_{He} stand for the respective masses of the hydrogen and the helium nuclei (M_H and M_{He} are practically the masses of the two *atoms*, since the masses of their electrons are negligible) and remembering that for helium $E = 2e$, we should have for the Rydberg constant for He and for H, respectively,

$$N_{He} = \frac{2\pi^2 me^4}{ch^3} \cdot \frac{M_{He}}{M_{He} + m} \tag{42a}$$

$$N_H = \frac{2\pi^2 me^4}{ch^3} \cdot \frac{M_H}{M_H + m} \tag{42b}$$

The atomic weight of hydrogen is 1.0077; that of helium, 4.00. From these values,

$$M_{He} = 3.969M_H$$

Making this substitution for M_{He} in equations (42), we have, by division,

$$\frac{N_{He}}{N_H} = \frac{1 + \dfrac{m}{M_H}}{1 + \dfrac{m}{3.969M_H}} \tag{43}$$

According to Sommerfeld,[1] the best values of N_{He} and N_H are, respectively, 109,722.14 and 109,677.69. Putting these values in

[1] "Atomic Structure and Spectral Lines," English translation, p. 224.

equation (43) and solving for m/M_H gives, for the ratio of the mass of the electron to that of the hydrogen atom,

$$\frac{m}{M_H} = \frac{1}{1{,}846}$$

This value of the ratio of these two masses is practically identical with that determined by other methods. For example, Sharp,[1] from measurements on the Compton effect in scattered X-rays, finds[2] that the mass of the electron is 8.99×10^{-28} grams. The mass M_H of the hydrogen atom, determined from Faraday's constant of electrolysis F, the atomic weight of hydrogen A, and the charge on the electron e, by the relation

$$M_H = \frac{A}{F/e}$$

is 1.663×10^{-24} grams. Hence, the ratio

$$\frac{m}{M_H} = \frac{8.99 \times 10^{-28}}{1.663 \times 10^{-24}} = \frac{1}{1{,}850}$$

Other methods for determining the ratio m/M_H give identical results within the limits of precision of the measurements.

(*d*) *Variation in the Rydberg Constant.*—This agreement between the value of m/M_H computed from the slight difference in the Rydberg constant for hydrogen and for helium and that determined by other methods is added confirmation of Bohr's theory. Further, equation (41) provides a method of computing the Rydberg constant for any element. Putting $E = Ze$, where Z is the atomic number of an element, we may write equation (41) in the form

$$n = Z^2 \cdot \frac{2\pi^2 me^4}{ch^3} \cdot \frac{M_z}{M_z + m} \cdot \left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right) \qquad (44)$$

where M_z stands for the mass of the nucleus of the element of atomic number Z. Evidently, the Rydberg constant N_z for this element is

$$N_z = \frac{2\pi^2 me^4}{ch^3} \cdot \frac{M_z}{M_z + m}$$

[1] *Phys. Rev.*, vol. 26, p. 691 (1925).

[2] The usual methods of determining the mass of the electron are based upon a measurement of e/m by any of the various methods (magnetic deflection, Zeeman effect, etc.) and a computation of m from the independently measured value of e. Sharp's method is independent of e/m but depends upon e, since the latter constant is used in measuring the wave length of the X-rays (see Chap. XII).

or,

$$N_Z = \frac{2\pi^2 me^4}{ch^3} \cdot \frac{1}{1 + \frac{m}{M_Z}} \quad (45)$$

We may write this in the form

$$N_Z = N_\infty \cdot \frac{1}{1 + \frac{m}{M_Z}} \quad (46)$$

where N_∞, given by

$$N_\infty \equiv \frac{2\pi^2 me^4}{ch^3} \quad (47)$$

is the value of the Rydberg constant for very large (practically infinite) values of M_Z. The constant N_∞ can, of course, be computed from equation (47); but the quantities involved are not known with spectroscopic precision. Rather, N_∞ is computed from equation (46) by using the observed value of N_Z, say, for hydrogen. From the observed value of N_H, namely 109,677.69, and the known ratio m/M_H, it is found that

$$N_\infty = 109{,}733.11$$

Using this value of N_∞ in equation (46), one can compute N_Z for any element. For example, taking the atomic weight of lithium ($Z = 3$) as 6.94, one finds that

$$N_{Li} = 109{,}724.51$$

For the heavier elements, N_Z approaches N_∞ within the limits of error of experiment.

(*e*) *The Rydberg-Schuster Law; Combination Lines.*—In Chap. IX, p. 308, we referred to the Rydberg-Schuster law that

> . . . the wave number of the first line of the principal series is equal to the difference between the convergence wave number of that series and the common convergence wave number of the sharp and the diffuse series.

Without, at this point, raising the question as to which of the series of lines predicted by the Bohr model of the atom is the principal, the sharp or the diffuse series, or how doublets and triplets arise in spectra, we see that the Bohr model at once suggests a law very similar to the Rydberg-Schuster law. For example, the Balmer series in hydrogen (see Fig. 92) originates from electrons dropping from outside orbits into orbit number 2. The convergence frequency ν_B of this series is given by electrons

dropping from infinity (*i.e.*, $\tau_2 = \infty$) to the second orbit, *i.e.*, by (see equation (31))

$$h\nu_B = 0 - W_2$$

where W_2 stands for the energy of the system for $\tau = 2$ (*i.e.*, the second orbit). In like manner, the convergence frequency ν_L of the Lyman series is given by

$$h\nu_L = 0 - W_1$$

Now the first line of the Lyman series is given by

$$\begin{aligned} h\nu_{1L} &= W_2 - W_1 \\ &= -h\nu_B + h\nu_L \\ \therefore \nu_{1L} &= \nu_L - \nu_B \end{aligned}$$

That is, the first line of the Lyman series is given by the difference between the convergence frequency ν_L of that series and the convergence frequency ν_B of the Balmer series. A similar relation exists between the first line of the Balmer series and difference between the convergence frequency of that series and the Paschen series. This result, extended, is the Rydberg-Schuster law.

In Sec. 6 of Chap. IX, mention was made of the existence of "combination" lines, which, while belonging to none of the recognized series, were characterized by the fact that the frequency of such lines was found equal to the difference in frequency of two other lines. Bohr's theory forms a ready picture of the production of such lines. For example, the frequency ν_{4B} of the fourth line of the Balmer series is given by

$$h\nu_{4B} = W_6 - W_2$$

and the frequency of the second line by

$$h\nu_{2B} = W_4 - W_2$$

Their difference in frequency is

$$h(\nu_{4B} - \nu_{2B}) = W_6 - W_4$$

This frequency difference should, therefore, be the frequency of the *second* line of the Brackett series (p. 258), the wave number of which is 3,800. The wave number of the fourth line of the Balmer series is 24,372 and of the second line, 20,564; and their difference is 3,808—equal, within the limit of measurement, to the wave number of the second line of the Brackett series.

8. Elliptical Orbits in Bohr's Theory.—(*a*) In the general case of motion under the action of a central force obeying the inverse

square law, such as the motion of a planet around a massive central sun or of an electron around a massive nucleus, the path is, as was shown by Newton, an ellipse with the central body at one of the foci. We have simplified the preceding discussion by considering only circular orbits. In this section, we shall discuss the more general case of elliptical orbits, partly to emphasize the physical principles involved and partly to extend the concept of quantum numbers. (The treatment is partly adapted from Sommerfeld's "Atomic Structure and Spectral Lines.")

In Fig. 94, let the path of the electron, charge e, mass m, around the nucleus, charge $+E$ and mass M, be the ellipse, the semimajor axis of which is a; the semiminor axis, b; and

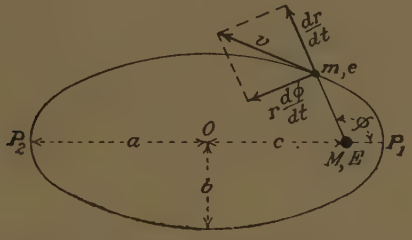


FIG. 94.—The motion of an electron in an elliptical orbit about a nucleus.

the eccentricity, $\epsilon = c/a$; O being the center of the ellipse, and the nucleus being at one focus which is distant c from O. Let the motion be described in terms of the two polar coordinates r and ϕ. At any instant when the tangential velocity is v the momentum is mv. This velocity v has components: (1) v_r, a radial component equal to dr/dt (or, more conveniently, $\dot{r}$), and (2) a component at right angles thereto, equal to $r\dfrac{d\phi}{dt}$ (or $r\dot{\phi}$). Likewise, corresponding to the two coordinates we have two momenta: (1) a *radial* momentum p_r given by

$$p_r = m\dot{r} \tag{48a}$$

and (2) an *angular* momentum p_ϕ given by

$$p_\phi = mr^2\dot{\phi} \tag{48b}$$

The radial momentum p_r varies throughout the cycle: p_r is zero at point P_1; will then reach a maximum; and will become zero again at point P_2. If, however, we grant (1) that the electron does not radiate as it traverses the orbit and (2) *that the mass* m of the electron remains constant throughout the orbit

(*i.e.*, does not vary with velocity—we shall consider the general case later), it is obvious that p_ϕ must remain constant, since the force on the electron is always directed toward M, and, therefore, *there is no component of force at right angles to r*

(*b*) Now, Sommerfeld assumes that to *each* of these momenta p_r and p_ϕ we may apply the phase integral (equation (18))

$$\oint pdq = \tau h \tag{18}$$

as follows:

$$\oint p_\phi d\phi = \tau_\phi h \tag{49a}$$

$$\oint p_r dr = \tau_r h \tag{49b}$$

where τ_ϕ is an *angular* or *azimuthal* quantum number and τ_r is a *radial* quantum number. If the *state* of the atom is defined by a *total* quantum number τ (identical with the quantum number which we have considered in previous sections for circular orbits, for which, of course, $\tau_r = 0$, since the radial momentum is zero for circular orbits), these three quantum numbers are related by the equation

$$\tau = \tau_\phi + \tau_r \tag{50}$$

For a given state corresponding to total quantum number τ, τ_ϕ and τ_r may have various (integer) values, but their *sum* must always be equal to τ. The significance of this will appear presently.

Introducing the values of p_r and p_ϕ, from equations (48), into equations (49), we have

$$\oint mr^2\dot{\phi}d\phi = \tau_\phi h \tag{51a}$$

$$\oint m\dot{r}dr = \tau_r h \tag{51b}$$

Since, as we have just seen, $mr^2\dot{\phi}$ is constant, we can, at once, integrate equation (51*a*). We then have

$$2\pi p_\phi = \tau_\phi h$$

$$\therefore p_\phi = \tau_\phi \cdot \frac{h}{2\pi} \tag{52}$$

(Compare with equation (20).)

Equation (51*b*) is not so easily integrated, since it contains *two* variables r and $\dot{r}$. We shall use the properties of the ellipse and the equation (52) to express both of these variables in terms of the coordinate ϕ. A relation between r and ϕ for the ellipse is given by

$$\frac{1}{r} = \frac{1 + \epsilon \cos \phi}{a(1 - \epsilon^2)} \tag{53}$$

where a is the semimajor axis and ϵ is the eccentricity. The semiminor axis b is

$$b = a\sqrt{1 - \epsilon^2}$$

We shall, also, need to use the value of $1/r \cdot dr/d\phi$. From equation (53), we find

$$\frac{dr}{d\phi} = \frac{a(1 - \epsilon^2)\epsilon \sin \phi}{(1 + \epsilon \cos \phi)^2} \tag{54}$$

Multiplying this by $1/r$ from equation (53), we have

$$\frac{1}{r} \cdot \frac{dr}{d\phi} = \frac{\epsilon \sin \phi}{1 + \epsilon \cos \phi} \tag{55}$$

From equations (48) we have a relation between p_r and p_ϕ, given by

$$p_r = p_\phi \cdot \frac{\dot{r}}{r^2\dot{\phi}} = p_\phi \cdot \frac{1}{r^2}\frac{dr}{d\phi} \tag{56}$$

For dr we may write,

$$dr = \frac{dr}{d\phi} d\phi \tag{57}$$

Inserting into equation (49*b*) these values of p_r and dr from equations (56) and (57) gives

$$\oint p_\phi \cdot \frac{1}{r^2}\frac{dr}{d\phi} \cdot \frac{dr}{d\phi} d\phi = \tau_r h$$

$$\therefore p_\phi \oint \left(\frac{1}{r}\frac{dr}{d\phi}\right)^2 d\phi = \tau_r h \tag{58}$$

By use of equations (52) and (55), we have, from equation (58),

$$\frac{\epsilon^2}{2\pi} \oint \frac{\sin^2 \phi}{(1 + \epsilon \cos \phi)^2} d\phi = \frac{\tau_r}{\tau_\phi} \tag{59}$$

We now have a single variable ϕ under the integral. Integrating this equation by parts,[1] we obtain, first,

$$\frac{\tau_r}{\tau_\phi} = \left[\frac{\epsilon}{2\pi}\frac{\sin\phi}{1+\epsilon\cos\phi}\right]_0^{2\pi} - \frac{\epsilon}{2\pi}\int_0^{2\pi}\frac{\cos\phi}{1+\epsilon\cos\phi}d\phi. \qquad (60)$$

The term in brackets is zero for both limits, and there remains

$$\frac{\tau_r}{\tau_\phi} = -\frac{\epsilon}{2\pi}\int_0^{2\pi}\frac{\cos\phi}{1+\epsilon\cos\phi}\,d\phi \qquad (61)$$

Equation (61) readily takes the form

$$\frac{\tau_r}{\tau_\phi} = \frac{1}{2\pi}\int_0^{2\pi}\left(\frac{1}{1+\epsilon\cos\phi} - 1\right)d\phi \qquad (62)$$

After integration[2]

$$\frac{\tau_r}{\tau_\phi} = \frac{1}{\sqrt{1-\epsilon^2}} - 1$$

Therefore,

$$1-\epsilon^2 = \left(\frac{\tau_\phi}{\tau_\phi+\tau_r}\right)^2 \qquad (63)$$

$$\therefore \epsilon = \sqrt{1-\left(\frac{\tau_\phi}{\tau_\phi+\tau_r}\right)^2} \qquad (64)$$

Equation (64) shows us that, for a given value of the total quantum number $\tau = \tau_\phi + \tau_r$, the number of possible ellipses is not infinite but is limited by the number of possible values of τ_ϕ. If $\tau = \tau_\phi + \tau_r = 4$, for example, 4 different ellipses are possible. 1 for each of the values of $\tau_\phi = 1, 2, 3,$ or 4. For $\tau_\phi = 0$, the eccentricity would be 1, and the path of the electron would be a straight line *through* the nucleus. This value of τ_ϕ is, therefore, ruled out. We can more readily interpret equation (64) further after computing the energy W of the system corresponding to the various elliptical orbits.

(*c*) The energy W of the system when the electron is at some such point in its orbit as is represented in Fig. 94, is partly potential U, and partly kinetic T. The total energy W is

$$W = T + U \qquad (65)$$

[1] In the standard equation $\int udv = uv - \int vdu$, let

$$u = \sin\phi \text{ and } dv = \frac{\sin\phi}{(1+\epsilon\cos\phi)^2}d\phi.$$

[2] See any standard table of integrals.

The potential energy when the electron is at a distance r from the nucleus is, as in equation (24),

$$U = -\frac{Ee}{r} = -\frac{Ee}{a} \cdot \frac{1 + \epsilon \cos \phi}{1 - \epsilon^2} \tag{66}$$

by equation (53). The kinetic energy is

$$T = \tfrac{1}{2}m\dot{r}^2 + \tfrac{1}{2}m(r\dot{\phi})^2 \tag{67}$$

We wish to express T in terms of ϕ only. By multiplying and dividing the first term on the right-hand side of equation (67) by m and the second term by mr^2, and factoring, we have

$$T = \frac{1}{2m}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right) \tag{68}$$

Substituting for p_r, by equation (56), gives

$$T = \frac{p_\phi^2}{2m} \cdot \frac{1}{r^2}\left[\left(\frac{1}{r}\frac{dr}{d\phi}\right)^2 + 1\right] \tag{69}$$

By use of equations (53) and (55), equation (69) readily reduces to

$$T = \frac{p_\phi^2}{2ma^2} \frac{\epsilon^2 + 2\epsilon \cos \phi + 1}{(1 - \epsilon^2)^2} \tag{70}$$

We can now write the expression for the total energy of the system,

$$W = T + U = \frac{p_\phi^2}{2ma^2} \cdot \frac{\epsilon^2 + 2\epsilon \cos \phi + 1}{(1 - \epsilon^2)^2} - \frac{Ee}{a} \cdot \frac{1 + \epsilon \cos \phi}{1 - \epsilon^2} \tag{71}$$

(*d*) Now, *granting that there is no radiation*, the *energy* of the system is constant for all values of ϕ. Therefore,

$$\frac{dW}{d\phi} = 0$$

Differentiating equation (71), we have

$$\frac{dW}{d\phi} = 0 = -\frac{p_\phi^2}{2ma^2} \cdot \frac{2\epsilon \sin \phi}{(1 - \epsilon^2)^2} + \frac{Ee}{a} \cdot \frac{\epsilon \sin \phi}{1 - \epsilon^2} \tag{72}$$

Solving this equation for a gives

$$a = \frac{p_\phi}{mEe(1 - \epsilon^2)} \tag{73}$$

Inserting the values of p_ϕ and of $(1 - \epsilon^2)$ from equations (52) and (63), respectively, we finally have for a, the semimajor axis of the ellipse,

$$a = (\tau_\phi + \tau_r)^2 \frac{h^2}{4\pi^2 mEe} \tag{73'}$$

This equation, comparable with equation (28), shows that the semimajor axis of the ellipse depends only on the *sum* of the two quantum numbers and is, therefore, the same for all ellipses (including the circle) of the same *total* quantum number τ, irrespective of the particular values of τ_ϕ and τ_r.

The semiminor axis b, however, depends on the azimuthal quantum number τ_ϕ. For, since

$$b = a\sqrt{1 - \epsilon^2}$$

we find

$$b = \tau_\phi(\tau_\phi + \tau_r)\frac{h^2}{4\pi^2 mEe} \tag{74}$$

For a given total quantum number τ, therefore, the semiminor axis b is proportional to the azimuthal quantum number τ_ϕ. The perihelion distance $d = (a - c)$ (Fig. 94) is given by

$$\begin{aligned} d &= a(1 - \epsilon) \\ &= (\tau_\phi + \tau_r)^2\frac{h^2}{4\pi^2 mEe}\left(1 - \sqrt{1 - \frac{\tau_\phi^2}{(\tau_\phi + \tau_r)^2}}\right) \end{aligned} \tag{75}$$

For a given total quantum number $(\tau_\phi + \tau_r)$, the perihelion distance d becomes smaller the smaller the value of τ_ϕ.

(*e*) Returning to equation (71) for W, inserting therein the value of $\frac{p_\phi^2}{ma}$ as determined from equation (73), we obtain

$$\begin{aligned} W &= \frac{Ee}{a(1 - \epsilon^2)}\left[\frac{\epsilon^2 + 2\epsilon\cos\phi + 1}{2} - (1 + \epsilon\cos\phi)\right] \\ &= \frac{Ee}{a(1 - \epsilon^2)} \cdot \frac{\epsilon^2 - 1}{2} \\ &= -\frac{Ee}{2a} \end{aligned} \tag{76}$$

In other words, *the energy W of the system depends only on the major axis $2a$ of the ellipse, and since*, as we have seen, this major axis depends only on the *total* quantum number, the *energy of the system is the same for all ellipses having the same total quantum number*. By putting into equation (76) the value of a determined by equation (73′), we finally have, for W,

$$W = -\frac{2\pi^2 mE^2e^2}{h^2} \cdot \frac{1}{(\tau_\phi + \tau_r)^2} \tag{77}$$

Introducing, as before, Bohr's postulate that, when the system changes from a state designated by the total quantum number

τ_2 to a state of lower energy designated by τ_1, $(\tau_2 > \tau_1)$, a quantum of energy $h\nu$ is radiated the magnitude of which is given by

$$h\nu = W_{\tau_2} - W_{\tau_1}$$

we obtain, for the frequency of radiation (we change to wave number n),

$$n = \frac{2\pi^2 mE^2e^2}{ch^3}\left[\frac{1}{(\tau_\phi + \tau_r)_1^2} - \frac{1}{(\tau_\phi + \tau_r)_1^2}\right] \tag{78}$$

where the subscripts refer to the two different states. The value of τ_ϕ and τ_r in $(\tau_\phi + \tau_r)_1$ may assume any integer values so long as $(\tau_\phi + \tau_r)_1 = \tau_1$; and so for $(\tau_\phi + \tau_r)_2$

For given values of the total quantum numbers τ_1 and τ_2, this equation is *numerically* identical with equation (41),

$$n = \frac{2\pi^2 mE^2e^2}{ch^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right) \tag{41}$$

derived from a consideration of circular orbits only. The *extension of the discussion to elliptical orbits, therefore, has apparently introduced no new frequencies.* The significance of equation (78), however, lies rather in the fact that it emphasizes the importance of the *two* quantum number τ_ϕ and τ_r introduced to describe in quantum terms the more general case of elliptical orbits. The various possible orbits for total quantum numbers 1, 2, 3, and 4, respectively, are shown in Table VI. The column headed

TABLE VI.—POSSIBLE ORBITS FOR VARIOUS AZIMUTHAL AND RADIAL QUANTUM NUMBERS

τ	τ_ϕ	τ_r	Orbit and designation	Major axis	Minor axis	Eccentricity
1	1	0	Circle 1_1	a	a	0
2	2	0	Circle 2_2	$4a$	$4a$	0
2	1	1	Ellipse 2_1	$4a$	$2a$	$\frac{1}{2}\sqrt{3}$
3	3	0	Circle 3_3	$9a$	$9a$	0
3	2	1	Ellipse 3_2	$9a$	$6a$	$\frac{1}{3}\sqrt{5}$
3	1	2	Ellipse 3_1	$9a$	$3a$	$\frac{1}{3}\sqrt{8}$
4	4	0	Circle 4_4	$16a$	$16a$	0
4	3	1	Ellipse 4_3	$16a$	$12a$	$\frac{1}{4}\sqrt{7}$
4	2	2	Ellipse 4_2	$16a$	$8a$	$\frac{1}{4}\sqrt{12}$
4	1	3	Ellipse 4_1	$16a$	$4a$	$\frac{1}{4}\sqrt{15}$

"Designation" is in a terminology, now largely superseded but useful for our purpose, in which the azimuthal quantum number τ_ϕ appears as a subscript to the total quantum number τ. Thus, the orbit 4_2 represents the orbit with total quantum number 4 and azimuthal quantum number 2.[1]

When the atom is in the state designated by $\tau = 4$, the electron may occupy any one of the four orbits. For $\tau = 2$, there are two orbits. So far as anything which we have said up to the present is concerned, transitions from the state $\tau = 4$ to the state $\tau = 2$ could take place in any one of *eight* different ways: from each one of the *four* orbits for $\tau = 4$ to each one of the two orbits for $\tau = 2$. According to *our assumptions*, namely, (1) that the atom does not radiate while the electron is revolving in a privileged orbit and (2) that the mass of the electron is constant and independent of velocity, all orbits for a given quantum number should have the same energy (equation (77)). And, therefore, these eight transfers should, as mentioned in the preceding paragraph, result in the emission of identical frequencies. We shall see in the next section, however, that the second of these two assumptions is not justified.

9. Fine Structure of Spectral Lines.—(*a*) It has long been known, both from experimental results and from theoretical considerations, that the mass of bodies should depend on their velocity. Many years ago, Sir J. J. Thomson showed that, on the hypothesis that the mass of the electron is of electromagnetic origin, the mass should increase with velocity. The variation of mass computed by Thomson[2] on this hypothesis was in qualitative agreement with the experiments of Kaufmann,[3] who measured the values of e/m for the high-velocity electrons ejected by radioactive substances. Not until the velocity becomes an appreciable fraction of the velocity of light, however, is there any measureable increase in the mass.

Later, it was shown that, on the principle of relativity, an increase in mass with velocity is to be expected, and Lorentz

[1] The reader will find it instructive to sketch these families of ellipses to scale and in correct relative positions around a central nucleus. The absolute value of a, say for the hydrogen atom, is given by putting the known quantities in equation (73′).

[2] See, for a brief account, THOMSON: "Corpuscular Theory of Matter."

[3] *Ann. Physik*, vol. 29, p. 487 (1906).

computed that the mass m of an electron moving with velocity v should be

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad (79)$$

where m_0 is the "rest" mass, *i.e.*, the mass for very small velocities, and c is the velocity of light. This expression for the variation of mass with velocity is much simpler than the one deduced from the electromagnetic hypothesis of the variation of mass and leads to slightly different results. There has been much controversy and much weighing of both theoretical and experimental evidence to decide whether the relativity law of variation of mass is the correct one. For our purpose, the important point is that, *qualitatively*, a variation of mass with velocity is to be expected, *irrespective of the principle of relativity*. The expression "relativity change of mass" should, therefore, refer to the particular *formulæ* used to compute masses at various velocities rather than to the *origin of the phenomenon*.

(*b*) Now, in the elliptical orbits to which we have referred in the preceding section, the velocity of the electron varies considerably at different points in the orbit: the velocity varies from a maximum when the electron is nearest the nucleus, *i.e.*, when the radius vector r is a minimum, to a minimum when r is a maximum. If we admit the constancy of angular momentum;

$$mr^2\frac{d\phi}{dt} = \text{constant}$$

Kepler's law of equal areas swept over by the radius vector in equal times follows at once. For, the area dA swept over in a time dt during which the radius advances $d\phi$ is

$$dA = \tfrac{1}{2}r^2 d\phi$$

and it follows that

$$2m\frac{dA}{dt} = \text{constant}$$

as long as m is constant. If, however, m varies from point to point in the path on account of the variation of velocity, conditions are quite different, and it turns out that the path is no longer an ellipse; is, indeed, no longer a closed figure but is somewhat as shown in Fig. 95, which represents diagrammatically an elliptical path referred to a major axis which rotates in the

plane of the figure about one of the foci as a center at such an angular velocity as to cause an advance (of the axis) between successive maximum values of the radius vector r through an angle P_1MP_2, the advance being in the same angular direction as the motion of the electron around the nucleus. We might describe the path by saying that it is equivalent to an ellipse in which the radius vector between its successive maximum values, instead of sweeping through an angle 2π, as in the ellipse proper, sweeps through an angle $(2\pi + \angle P_1MP_2)$ or, more generally, through the angle $2\pi/\gamma$ where γ is a quantity less than unity. The equations of the ellipse, such as those given on page 367

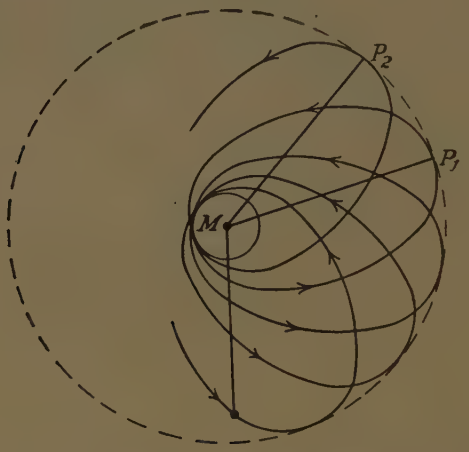


FIG. 95.—The effect of variation of mass with velocity on the motion of an electron in an eccentric orbit around a nucleus.

may be retained, if, in place of ϕ, is written $\gamma\phi$. Sommerfeld shows[1] that γ is given by

$$\gamma = \sqrt{1 - \frac{E^2e^2}{p_\phi^2c^2}}$$

the quantities having the meanings previously assigned to them.

(*c*) We see that the motion of the electron now involves *two* periodicities: one, the period of the variation of the radius vector between successive maxima; the other, the period of rotation of the axis around M as a center. Since the quantity γ differs by only a small amount from unity, the second of these two periods is much longer than the first. We, therefore, have a motion of the

[1] "Atomic Structure and Spectral Lines," Chap. VIII.

electron somewhat similar to that discussed in connection with the Zeeman effect, on page 322. And if the electron, in describing this path, were to radiate according to *classical* laws, we should expect to find in the emitted radiation *two slightly different* frequencies. The quantum theory predicts somewhat similar results but gives a very different "picture" of the phenomenon. The results of an analysis due to Sommerfeld[1] are, briefly, as follows:

Starting with the equations of the ellipse similar to those given on page 146 but with $\gamma\phi$ substituted for ϕ, and following a line of development similar to that used above for elliptical orbits, Sommerfeld first deduces a value for the energy W of the system for a given quantum state τ, assuming the mass of the electron to vary with velocity according to equation (79). His final equation for W (analogous to equation (77) but very different in form) is

$$W = -m_0c^2 + m_0c^2\left[1 + \frac{(\alpha Z)^2}{[\tau_r + \sqrt{\tau_\phi^2 - (\alpha Z)^2}]^2}\right]^{-\frac{1}{2}} \qquad (80)$$

where m_0 is the "rest mass" of the electron (previously called m), $\alpha \equiv 2\pi e^2/ch$, Z is the nuclear charge, and the other quantities have meanings as previously assigned to them.

For comparison[2] with the equation (77),

$$W = -\frac{2\pi^2 mE^2e^2}{h^2}\frac{1}{(\tau_r + \tau_\phi)^2} \qquad [77]$$

which is the equation for W derived by disregarding variation of mass with velocity, we may change equation (80) as follows: For simplicity in writing, put

$$(\alpha Z) \equiv \rho$$
$$\tau_r + \sqrt{\tau_\phi^2 - (\alpha Z)^2} \equiv S$$

Equation (80) then takes the form[3]

$$W = -m_0c^2 + m_0c^2\left[1 + \frac{\rho^2}{S^2}\right]^{-\frac{1}{2}}$$
$$= -m_0c^2 + m_0c^2\left[1 - \frac{1}{2}\frac{\rho^2}{S^2} + \frac{3}{8}\frac{\rho^4}{S^4} - \cdots\right]$$

[1] *Loc. cit.*
[2] Remember that $E = Ze$.
[3] $(a + x)^n = a^n + na^{n-1}x \cdots$

in which we may neglect terms of higher order, since $\frac{\rho^2}{S^2} \ll 1$. Since

$$[\tau_\phi^2 - (\alpha Z)^2]^{\frac{1}{2}} = \tau_\phi - \frac{1}{2}\frac{\rho^2}{\tau_\phi} \cdots$$

$$\therefore \frac{1}{S} = \frac{1}{(\tau_r + \tau_\phi) - \frac{1}{2}\frac{\rho^2}{\tau_\phi}}$$

$$\therefore \frac{1}{S^2} = \frac{1}{(\tau_r + \tau_\phi)^2} + \frac{1}{(\tau_r + \tau_\phi)^3}\frac{\rho^2}{\tau_\phi} \cdots$$

$$= \frac{1}{(\tau_r + \tau_\phi)^2} + \frac{\rho^2}{(\tau_r + \tau_\phi)^4} \cdot \frac{\tau_r + \tau_\phi}{\tau_\phi} \cdots$$

and

$$\frac{1}{S^4} = \frac{1}{(\tau_r + \tau_\phi)^4} \cdots$$

Putting into the above equation for W these values of $1/S^2$ and $1/S^4$ (in all of which we neglect terms of higher order than ρ^4/S^4) and replacing ρ and S by their equivalents, we have, after simplifying[1]

$$W = -\frac{2\pi^2 m Z^2 e^4}{h^2}\left[\frac{1}{(\tau_r + \tau_\phi)^2} + \frac{4\pi^2 Z^2 e^4}{c^2 h^2}\left(\frac{\tau_r + \tau_\phi}{\tau_\phi} - \frac{3}{4}\right)\frac{1}{(\tau_r + \tau_\phi)^4}\right] \tag{80'}$$

This equation is seen to differ from equation (77) in that it contains a *second* term within the square bracket, which term involves the *ratio* of the total quantum number $(\tau_r + \tau_\phi)$ to τ_ϕ. W, therefore, depends not simply on the *total* quantum number $(\tau_r + \tau_\phi)$, as in equation (77), but also on how the total quantum number is distributed between τ_ϕ and τ_r. Thus, for total quantum number 3, the parenthesis within the square bracket may have any one of the three following values:

$$\text{For } \tau_\phi = 3 \text{ and } \tau_r = 0\text{:} \quad \frac{\tau_r + \tau_\phi}{\tau_\phi} - \frac{3}{4} = \frac{3}{3} - \frac{3}{4} = \frac{1}{4}$$

$$\text{For } \tau_\phi = 2 \text{ and } \tau_r = 1\text{:} \quad \frac{\tau_r + \tau_\phi}{\tau_\phi} - \frac{3}{4} = \frac{3}{2} - \frac{3}{4} = \frac{3}{4}$$

$$\text{For } \tau_\phi = 1 \text{ and } \tau_r = 2\text{:} \quad \frac{\tau_r + \tau_\phi}{\tau_\phi} - \frac{3}{4} = \frac{3}{1} - \frac{3}{4} = \frac{9}{4}$$

[1] We drop the subscript of m in equation (80'); *i.e.*, m in equation (80') is the "rest mass" of the electron.

W is (algebraically) smaller the smaller τ_ϕ, for a given value of $(\tau_r + \tau_\phi)$. In other words, an ellipse of given total quantum number τ represents an orbit of *lower* energy level than the corresponding circle; and the greater the eccentricity of the ellipse the lower the level.

Consequently, an electron dropping from some given outside orbit into the ellipse $\tau_\phi = 1$, $\tau_r = 1$ *will emit a frequency slightly different from that emitted by an electron in dropping from the same outside orbit into the circle* $\tau_\phi = 2$, $\tau_r = 0$. The *difference* in these two frequencies is determined by the *difference* in the energies for the two states of quantum number 2. More specifically, let W_{2_2} (the subscript 2_2 designates the circular orbit, as in the terminology for orbits given in Table VI) be the energy corresponding to the circular orbit 2_2; and W_{2_1} the same for the elliptical orbit 2_1; and let W_τ be the energy corresponding to some given outside orbit τ. Then, the frequency ν_{2_2} corresponding to the transition $\tau \rightarrow 2_2$ is given by Bohr's quantum postulate

$$h\nu_{2_2} = W_\tau - W_{2_2} \tag{81a}$$

and, similarly,

$$h\nu_{2_1} = W_\tau - W_{2_1} \tag{81b}$$

The difference in the two frequencies is given by

$$h(\nu_{2_2} - \nu_{2_1}) = W_{2_1} - W_{2_2} \tag{82}$$

To illustrate: The Balmer series in hydrogen originates in transitions from outside orbits into either of the two orbits corresponding to $\tau = 2$. The frequency of a given line, therefore, should be slightly different according as the electron falls into the ellipse or the circle. *In other words, the lines of the Balmer series should be doublets*, close doublets, since the difference in energy of the two orbits is not very great. Spectral lines made up of such components of slightly different frequency are said to have a "fine structure."

Sommerfeld shows that, neglecting small, second-order quantities (which, however, are of importance in the heavier elements), the *difference* in wave number Δn arising from the difference in energy between two such orbits (more correctly, "states") of the same total quantum number τ but of different azimuthal

quantum numbers τ_ϕ and radial quantum numbers τ_r should be given by[1]

$$\Delta n = R_\infty \frac{\alpha^2 Z^4}{\tau^4}\left[\left(\frac{\tau_r}{\tau_\phi}\right)_1 - \left(\frac{\tau_r}{\tau_\phi}\right)_2\right] \tag{83}$$

where R_∞ is the Rydberg constant[2]; $\alpha \equiv \frac{2\pi e^2}{ch}$; Z is the atomic number of the element; τ is the total quantum number; and the subscripts refer to the different distributions of τ_r and τ_ϕ, subject to $\tau = \tau_r + \tau_\phi$.

(*d*) Let us apply equation (83) to the Balmer series in hydrogen ($Z = 1$) which originates in the "dropping" of electrons from outside orbits into either the circle of quantum number 2 or the ellipse of quantum number 2. For the circle $\tau_\phi = 2$ and $\tau_r = 0$; for the ellipse, $\tau_\phi = 1$ and $\tau_r = 1$. We, therefore, have

$$\begin{aligned}\Delta n_{\mathrm{H}} &= R_\infty \alpha^2 (1/2)^4 [1/1 - 0/2] \\ &= R_\infty \frac{\alpha^2}{2^4} = 0.365\,\mathrm{cm.}^{-1}\end{aligned} \tag{83'}$$

taking $R = 109{,}700$; $e = 4.77 \cdot 10^{-10}$ e.s.u.; $c = 3 \cdot 10^{10}$ cm.sec.$^{-1}$; $h = 6.55 \cdot 10^{-27}$ erg. sec. This gives the difference in wave number Δn_{H} to be expected between the two components of the several lines of the *Balmer series* if these lines are actually doublets. This difference in the case of H_α amounts to only about 3 parts in 150,000—about one-fiftieth of the distance between the sodium D lines. Nevertheless, in spite of very great experimental difficulties numerous investigations have shown that the lines of the Balmer's series *are* actually close doublets and that the difference in wave number between the two components is of the order of that predicted by Sommerfeld's theory. Sommerfeld (*loc. cit.*, p. 482) quotes the following measurements for the difference in wave number between the components of the several lines:

[1] The derivation of this equation is left to the student. Starting with equation (80′) (analogous to equation (29), obtain an equation for n (analogous to equation (33′)). Equation (83) follows at once.

[2] See equation (47).

		CENTIMETERS^{-1}
Michelson	H_α:	$\Delta n_H = 0.32$
Michelson	H_β:	$= 0.33$
Fabry and Buisson	H_α:	$= 0.306$
Meissner and Paschen	H_α:	$= 0.288$
Gehrcke and Lau	H_α:	$= 0.272$
	H_β:	$= 0.283$
	H_γ:	$= 0.271$

To these may be added the more recent measurements of Shrum:[1]

	CENTIMETERS^{-1}
H_α:	$\Delta n_H = 0.33$
H_β:	$= 0.36$
H_γ:	$= 0.37$
H_δ:	$= 0.36$
H_ϵ:	$= 0.35$

Still more recently, W. V. Houstoun,[2] working with hydrogen at liquid-air temperature finds

	CENTIMETERS^{-1}
H_α:	$\Delta n_H = 0.315$
H_β:	$= 0.331$
H_γ:	$= 0.353$

There can, thus, be no doubt as to the *existence* of the effect. As to its magnitude, there has been considerable controversy, arising, in large part, from the theoretical importance attached to Sommerfeld's formula, coupled with the fact that many of the measurements quoted above tend to somewhat lower values than those predicted by equation (83′). In view of subsequent developments, such as the "spinning" electron of Uhlenbeck and Goudsmit and the wave theory of Schrödinger—which provide alternative explanations of fine structure and of many other spectral and atomic phenomena—it is pertinent to emphasize the *experimental* facts. Theories regarding those facts will ultimately become stabilized.

(*e*) One further comment, however, regarding the implications of Sommerfeld's equation (83) for fine structure may be in order. One of the experimental difficulties in making accurate measurements of Δn lies in the fact that the actual positions of the components of the several lines is made somewhat uncertain by the broadening of the spectral lines due to the Doppler effect. The magnitude of this effect depends on the mean velocities of

[1] *Proc. Roy. Soc.*, vol. 105, p. 259 (1924).

[2] *Astrophy. Jour.*, vol. 64, p. 81 (September, 1926).

the molecules or atoms of the gas. Even at liquid-air temperature, the theoretical width of the lines of the hydrogen spectrum is of the order of 0.05 Ångström, or one-seventh of the actual expected separation of the fine-structure components. The heavier the gas molecule, however, the less its velocity at a given temperature. And, further, equation (83) shows that Δn increases as the *fourth* power of the atomic number. The fine structures in the lines of helium should be subject to greater precision of measurement than corresponding lines in hydrogen, since $Z = 2$ for helium, which means a gain of 2^4 in separation (for the same quantum transfers as hydrogen); and the mass of the helium atom is four times that of the hydrogen atom, which means that, because of the smaller velocity of the helium atom at a given temperature, the Doppler broadening in helium should be approximately one-half that in hydrogen. Paschen[1] measured the Δn's for the components of the "4686" line of helium (of which there are five, see below) and, computing from these measurements the value of Δn_H (for hydrogen), found

$$\Delta n_H = 0.364 \pm 0.004 \text{ cm.}^{-1}$$

in complete agreement with Sommerfeld's prediction.

10. The Selection Principle.—The hydrogen line H_α arises from transitions from the quantum state $\tau = 3$ (three possible orbits) to the quantum state $\tau = 2$ (two possible orbits). Six different transfers from $\tau = 3$ to $\tau = 2$ might, therefore, be expected. We have seen that transfers from *any* outside orbit to the orbit $\tau = 2$ should result in a doublet. We might expect that H_α should be made up of *six* components or of *three* doublets, one doublet corresponding to each of the three orbits $\tau = 3$. We can represent these *mathematically* possible components of H_α in the schematic way shown in Fig. 96. The numbers are the quantum numbers of the respective orbits—the boldface numbers being the azimuthal quantum numbers, and the others the radial quantum numbers. Thus, the orbit "*2, 1*" is the orbit $\tau_\phi = 2$ and $\tau_r = 1$. For brevity in writing, we shall designate the orbits

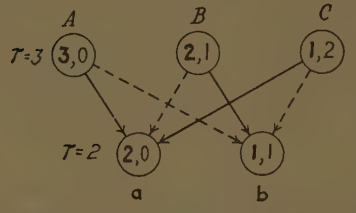


FIG. 96.—The origin of the six mathematically possible components of the hydrogen line H_α.

[1] *Ann. Physik*, vol. 50, p. 901 (1916).

by the letters A, B, C, a, b; and any given transfer by an obvious combination of the two letters; *e.g.*, "$A\ b$" represents the transfers from the orbit ***3***, *0* to the orbit ***1***, *1*. The arrows represent the six possible transfers. We shall see, presently, the reason for dotting some of the arrows.

From an equation for the wave number of a spectral line based on equations (80) and (81) we might compute the wave numbers of each of these six components. It will be simpler, however, to compute *differences* in wave numbers and to represent the location of each of the six components graphically from some one component as an arbitrary starting point. Using the equation (83)

$$\Delta n = \frac{R_\infty \alpha^2 Z^4}{\tau^4}\left[\left(\frac{\tau_r}{\tau_\phi}\right)_1 - \left(\frac{\tau_r}{\tau_\phi}\right)_2\right] \tag{83}$$

we can compute the difference in wave number Δn for any pair of transfers represented in Fig. 96. Thus, Δn_{Ab}^{Aa}, the difference in wave number between the lines Aa and Ab, is given by

$$\Delta n_{Ab}^{Aa} = R_\infty \alpha^2 Z^4 \cdot \frac{1}{2^4}\left(\tfrac{0}{2} - \tfrac{1}{1}\right) = -R_\infty \alpha^2 Z^4 \cdot \tfrac{1}{16} = -\ 0.365\ \text{cm.}^{-1}$$

and, similarly,

$$\Delta n_{Ca}^{Ba} = R_\infty \alpha^2 Z^4 \cdot \frac{1}{3^4}\left(\frac{2}{1} - \frac{1}{2}\right) = R_\infty \alpha^2 Z^4 \cdot \frac{3}{2 \cdot 81} = 0.110\ \text{cm.}^{-1}$$

In this way, we obtain data for Table VII, which shows the wave-number differences for a sufficient number of pairs to locate the components of H_α.

TABLE VII.—WAVE-NUMBER DIFFERENCES BETWEEN THE FINE-STRUCTURE COMPONENTS OF $H\alpha$

Δn	Multiplier of $R_\infty \alpha^2 Z^4$	$\Delta\nu$ in cm.$^{-1}$
Δn_{Ab}^{Aa}	$\frac{1}{16}\left(\frac{0}{2} - \frac{1}{1}\right)$	−0.365
Δn_{Bb}^{Ba}	$\frac{1}{16}\left(\frac{0}{2} - \frac{1}{1}\right)$	−0.365
Δn_{Cb}^{Ca}	$\frac{1}{16}\left(\frac{0}{2} - \frac{1}{1}\right)$	−0.365
Δn_{Ba}^{Aa}	$\frac{1}{81}\left(\frac{1}{2} - \frac{0}{3}\right)$	0.036
Δn_{Ca}^{Ba}	$\frac{1}{81}\left(\frac{2}{1} - \frac{1}{2}\right)$	0.108

From these wave-number differences, and starting with, say, the line Aa as an arbitrary origin, the position, on a wave-number scale, of the six components of H_α may be located as shown in Fig. 97. This is the mathematically possible fine structure of H_α. (The student will find it instructive to locate, in this way, the corresponding 8 components of H_β or the possible 12 components of the helium line "4686," which is made up of transfers from $\tau = 4$ to $\tau = 3$.)

Now, experimental evidence based upon observation on lines where one can obtain greater resolution than is possible in H_α shows that only a limited number of these mathematically possible lines are actually present. Rubinowicz, in 1918, from a consideration of the conservation of angular momentum as applied to the interchange of angular momentum between the atom and the emitted radiation during any interorbital transition, showed that in such a transition the azimuthal quantum number could change by only ± 1, no restriction, however, being made to the change in the radial quantum number. An identical conclusion has been reached by Bohr on quite different grounds. This limitation of the change in the azimuthal quantum number makes it possible, by ruling out the other changes, to "select" for any given line the components which ought to be present; hence, the name "*selection principle*," which states that *only those interorbital transfers are possible for which the change* $\Delta\tau_\phi$ *of the azimuthal quantum number is given by*

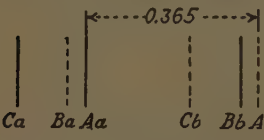


FIG. 97.—The observed components of the hydrogen line H_α. The dotted components are ruled out by the selection principle. The two left-hand components are so close together as to be observed spectroscopically as a single line.

$$\Delta\tau_\phi = \pm 1 \qquad (84)$$

The prohibited lines are those which are dotted in Figs. 96 and 97. For example, the line Ab (Fig. 96) is ruled out, since for it $\Delta\tau_\phi = 2$. The line Ca is permitted, since for it $\Delta\tau = -1$. The lines of the Balmer's series, therefore, should really be made of *three* components instead of only two, as discussed in the preceding section. Both experiment and theory show that not all of these three components have the same intensity, the component Ca (Fig. 97), for example, being much weaker than Aa and sufficiently close to Aa to prohibit separation spectroscopically. Measurements, therefore, give the center of gravity of these *two*

components, and the separation between this center and the component *Bb* is the "doublet" difference for the line H_α, *as actually measured.* For the higher components, H_β, H_γ, H_δ, etc., the separation between *Ca* and *Aa* become less, and the doublet difference as observed becomes more nearly that predicted, a conclusion in agreement with the measurements of Houstoun, quoted on page 379.

The reader, by application of the selection rule, can readily determine which components ought to be expected in other lines, say the helium line "4686,"[1] and can locate their relative positions.

The *selection principle*, which we have here applied to the azimuthal quantum number, has been extended to other quantum numbers to which we shall make reference in subsequent chapters.

11. Systems with More than 1 Electron.—Bohr's theory, in the simple elementary form, as presented in this chapter, is not applicable to atoms containing more than 1 electron revolving around the nucleus, since the presence of other electrons very materially affects the energy W corresponding to a particular orbit, or state. The mathematical difficulties of the famous "three body" problem prevent a rigorous extension of the Bohr equations for spectral series. Nevertheless, the Bohr theory has shown the way, partly by analogy, partly by empirical methods, for notable advances in the interpretation of spectral phenomena and their relation to atomic structure. Some of these we shall mention in the remaining articles of this chapter. Others we shall leave until later chapters, after we have considered some developments along other lines, particularly the evidence which led to the hypotheses concerning the distribution of electrons in atoms.

12. The Absorption of Energy by Atoms. (*a*) *Excitation and Ionization.*—In the preceding articles of this chapter, we have discussed the *emission* of characteristic radiation by atoms. In terms of Bohr's "picture" of the atomic mechanism, we have discussed the phenomena occurring when electrons "drop from outside orbits into inner orbits," the various orbits or, more generally, *stationary states* of the atom, being characterized by certain quantum numbers, which, together with certain constants, determine the energy W_τ corresponding to a given state τ. We

[1] For the actual measurements on this helium line, see PASCHEN: *Ann. Physik*, vol. 50, p. 901 (1916).

have pointed out that, by analogy with mechanical systems with which we are familiar, we should expect the *normal* state of the atom to be the state having the *lowest* energy. For the simple atom (*i.e.*, nucleus plus 1 electron), this is the state for which $\tau = 1$; or, again in terms of the "picture,"[1] the normal state of the simple atom is the state in which its electron is revolving in the innermost privileged orbit, the circle.

When, still speaking of the simple atom, the electron is revolving in orbits of higher quantum numbers than the normal orbit, the atom is said to be in an *excited* state, and the process of transferring the atom from the normal state to an excited state is referred to as *excitation.* It may happen that the excitation is so intense that the electron is completely removed from the nucleus. The atom is then left with a net positive charge and, if free, will tend to move in an electric field, like an ion in an electrolytic solution. Such an atom which has lost 1 electron (or more) is said to be in an *ionized* state, and the process of "raising" the atom from the normal state to the ionized state is called *ionization.*

[1] It should be emphasized that we should not take this picture of the atom with its several electrons revolving in the various "privileged" orbits too seriously, at least so far as concerns *the actual physical* makeup of an atom. The concept of orbits and of the "dropping of electrons from one orbit to another" is of value largely in helping us to keep in mind the *observed* phenomena and in suggesting other previously unknown phenomena which, in turn, suggest new experiments. It is probable that the picture of an atom with a planetary system of electrons is as far from the real architecture of the atom as are "lines of force" from the actual structure of the magnetic field. We find the concept of lines of force very useful in helping us to visualize certain phenomena. We compute electromotive forces by ascertaining the number of lines cut per second. Yet we know that, physically, there are no such lines in a magnetic field as we find it convenient to visualize. We do know, however, that *irrespective of any concrete picture of its structure, a magnetic field involves energy,* the amount of which per unit volume at any point we can compute by dividing a certain quantity H^2, characteristic of the field at the particular point, by 8π.

In a similar way, the concept of orbits, electron transfers, and the like is a very concrete and useful geometrical "picture" to help us keep in mind the various *states* of the atom. But whether the *picture* be correct or not, we are reasonably sure that the *energy* associated with these various stationary states is *real.* Sometimes it is more convenient to speak in terms of orbits; at other times, the more general phrase "energy corresponding to a given state" will be much more appropriate. We should always keep in mind, however, that the latter phraseology is physically justified; the former is quite artificial.

If, now, an atom is to radiate by a transfer from an excited (or an ionized) state to one of lower energy, the atom must first, by some means, be put in that excited state. That is, the atom must *absorb* energy sufficient to raise it from the normal to the excited state. This process of absorption is the converse of the process of radiation.

A full discussion of the entire subject of the excitation and ionization of atoms, and of the far-reaching conclusions drawn from experiments in this field, is quite beyond the scope of this book. The reader is referred to more exhaustive or special treatises on the subject. We may, however, make brief mention of some of the ways by which experiment shows that atoms may become excited or ionized and of the interpretation of some of these experiments.

(*b*) *Collisions between Atoms and Electrons or between Atoms and Other Atoms.*—The atoms of a gas (or vapor) may become excited

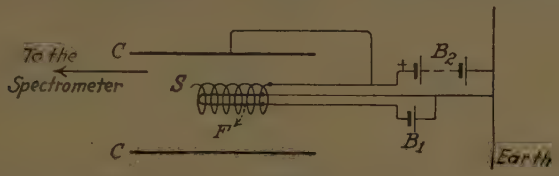


FIG. 98.—The apparatus of Foote, Meggers, and Mohler for studying excitation potentials.

or ionized by bombarding them with electrons possessed of *sufficient* kinetic energy. If the energy given to an atom by such a collision is sufficient to expel an electron from its normal orbit in the atom to infinity, the atom may become ionized. Otherwise, it becomes simply "excited." As one illustration of the mode of procedure followed in studying phenomena of this kind may be mentioned the experiments of Foote, Meggers, and Mohler.[1] Their apparatus is shown diagrammatically in Fig. 98. A filament F of tungsten or lime-coated platinum is heated, by a battery B_1, to such temperature that it emits electrons. Around the filament is a spiral grid S which, by means of a battery B_2 or potentiometric source of pd, is maintained at any desired *positive* potential with respect to the filament. Around S and electrically connected thereto is a metal cylinder CC; S and CC are thus at the same potential. Inside CC is the gas or vapor under study, maintained at a suitable pressure.

[1] See FOOTE and MOHLER: "The Origin of Spectra."

Electrons, emitted by the filament, are accelerated toward the grid S which is so close to F that with proper regulation of the gas pressure comparatively few atoms of the gas are struck by the electrons in their passage from filament to grid. After leaving the grid, the electrons move in the (electrical) force-free space between S and CC, in which space, because of the greater distance S to CC, the electrons collide with the gas molecules, causing the excitation of the latter, provided the velocity (energy) of the electrons is sufficiently great. With sodium vapor inside the cylinder, no luminosity is observed in the vapor until the potential difference between the grid and the filament reaches 2.09 volts. For voltages slightly above this value, the spectrograph shows that the sodium vapor emits the well-known D lines, *and those only*. The mean wave length of these lines is 5,893 Ångströms, corresponding to a *frequency* ν of $0.509 \cdot 10^{15}$ sec.$^{-1}$; the quantum energy $h\nu$ is $6.55 \cdot 10^{-27} \times 0.509 \cdot 10^{15} = 3.33 \cdot 10^{-12}$ ergs. According to the quantum picture of the origin of spectra, there must have been a change of *state* of the sodium atom, in *emitting* this line, corresponding to an *energy drop* of $3.33 \cdot 10^{-12}$ ergs—whatever may have been the *absolute* values of the energies in the initial and the final state. Now, the electrons, which, after emission from the filament, have dropped through 2.09 volts, have acquired a kinetic energy given by

$$eV = 4.77 \cdot 10^{-10} \times \frac{2.09}{3 \times 10^2} = 3.32 \cdot 10^{-12} \text{ ergs}$$

We see, therefore, that the kinetic energy possessed by the electrons as they pass through the space between the grid and the cylinder is *exactly* equal to the quantum energy of the radiation emitted by the sodium vapor. The presumption is very strong, therefore, that the electrons have, by collision, transferred to the sodium atoms sufficient energy to raise the latter from their *normal* state to an excited state $3.33 \cdot 10^{-12}$ ergs above the normal, so that the atoms in returning from that excited state to the normal state emit the line (doublet) $\lambda = \begin{cases} 5{,}896 \\ 5{,}890 \end{cases}$ Ångströms which, be it noted, is *the first line of the principal series of sodium* (see p. 299). We shall return to this latter point presently.

As the voltage between filament and grid is raised above 2.09 volts, the D lines continue to appear, but no others appear until the voltage reaches 5.12 volts, beyond which many more lines—in

fact, the complete arc spectrum—are produced. Beyond 35 volts, the so-called "spark" spectrum is seen. With these latter observations, important as they are, we are not now concerned. Let us consider a little further the significance of the observation (1) that up to 2.09 volts no emission of radiation occurs and (2) that above this voltage only the single pair of lines, the *D* lines, is produced until the voltage becomes considerably higher.

Electrons possessing energy equivalent to, say, 3.0 volts should, so far as *energy* is concerned, be able to communicate to sodium atoms sufficient energy to generate lines of wave length 4,100 Ångströms, or longer.[1] In the spectrum of sodium is found a large number of lines of longer wave length than this, for example practically the entire sharp and the diffuse series, the convergence wave length of which is of the order of 4,100 Ångströms. Why do not 3-volt electrons excite these lines? Or, the wave length of the second line of the sharp series is 6,161 Ångströms, corresponding to about 2.01-volt electrons. Why is this line not produced at lower voltages than the *D* lines which correspond to 2.09 volts?

We can more adequately answer these questions after considering, further, the various excited states of the sodium atom and their relation to the several known spectral series, as viewed in the light of the arrangement, in the sodium atom, of the 11 electrons which it is known to contain. A clue to the answers to the above questions, however, is furnished by considering the stationary states of the simple (hydrogen) atom (nucleus plus 1 electron), as represented by the circular orbits in Fig. 92.

It may be assumed that, *normally*, the electron of the hydrogen atom will be in the lowest level, the circle $\tau = 1$. In order that the atom may be excited so as to radiate, it must be given *at least*

[1] Assuming that the quantum energy $h\nu$ of the emitted lines is equal to the energy acquired by the electron in falling through V volts, we have

$$Ve = h\nu = h\frac{c}{\lambda}$$

$$\lambda = \frac{ch}{Ve}$$

In this formula, V is to be expressed in electrostatic units of potential difference, which are given by $\frac{\text{volts}}{3 \times 10^2}$. If V is kept in volts and the numerical values of c, h, and e are inserted, we find for λ the expression, convenient to remember,

$$\lambda = \frac{12{,}345}{V} \text{ Ångströms.}$$

a sufficient quantity of energy so that the electron will be raised to the second orbit $\tau = 2$. The electron may then drop back to the first orbit and, in so doing, emit the *first* line of the Lyman series ($\lambda = 1{,}216$ Ångströms), which, computing as above, should require about 10-volt electrons. Electrons possessing less energy than that corresponding to 10 volts, if they were to collide with normal atoms, could not raise the atom from the normal to the *first* excited state, and they could, therefore, excite no radiation. To such collisions, in which the atom receives no energy from the electron, is applied the term "elastic," by analogy with mechanical systems; while collisions in which the atom is raised from one state, say the normal, to another, are called *inelastic* collisions.

To raise the electron from the first orbit to the third (Fig. 92) should require some *twelve* volts. (The wave length of the second line of the Lyman series is 1,026 Ångströms.) Once the electron is in the third orbit, it could return to the normal state either by dropping to the second orbit (thereby producing the first line of the Balmer series) and thence to the normal orbit, or it might go *directly* from the third orbit to the first. We see then, that, although the wave length of the first line of the Balmer series ($\lambda = 6{,}563$ Ångströms) is such as to correspond to an energy transfer in the atom equivalent to only about *two* volts, this line could not be produced unless electrons corresponding to at least 12 volts were to collide with the normal atom.

Returning to the experiments with sodium vapor and assuming that the sodium atoms before collision with the 2.09-volt electrons were in the normal state, we conclude that the impact with the 2.09-volt electrons was sufficient to raise the sodium atom from the normal state to the *first* excited state above normal. On returning from that excited state the atoms emit the *D* line—*the first line of the principal series.* Continuing the analogy with hydrogen, before the sodium atom can emit any other line than the first line of the principal series it (the atom) must be raised to some *higher* stationary state than the second. This requires *more* than 2.09 volts.

In passing, we may call attention to the fact that the excitation of the *D* lines does not cease when the voltage *exceeds* 2.09 volts, but continues at higher voltages.

We are now also in position to point out the significance of the observation that with sodium vapor the entire arc spectrum of the element is emitted when the potential difference between

filament and grid exceeds 5.12 volts. The convergence wave number of the principal series of sodium is 41,450, wave length 2,410 Ångströms. Electrons falling from infinity to the normal state should generate this frequency, the quantum energy value of which is

$$h\nu = 6.55 \cdot 10^{-27} \times 41{,}450 \times 3 \cdot 10^{10} = 8.15 \cdot 10^{-12} \text{ ergs.}$$

Conversely, electrons possessing this amount of kinetic energy, which energy should result from their falling through 5.12 volts (between filament and grid), should, by collision with sodium atoms, impart to the atoms sufficient energy to raise an electron in the sodium atom to infinity: *i.e.*, to *ionize* the atom. In returning to its normal orbit this electron might "drop" into any of the intervening privileged orbits and therefore generate the entire (arc) spectrum of sodium. In other words 5.12 volts is the *ionization* potential of the sodium atom.

(*c*) *Excitation by Radiation.*—On the classical theory, the characteristic frequencies emitted by an atom should be identical with, or overtones of, the natural frequencies of the vibrating "systems" of which the atoms are composed. These "systems" should, according to the familiar principle of resonance, absorb (*i.e.*, resonate with) radiation of identical frequencies; and, thus being set into vibration, the atom should re-emit these same frequencies. Confirmation of this view of resonance absorption was apparently to be found in the well known phenomenon of the "reversals" of spectrum lines, of which phenomena the most conspicuous are the dark lines in the solar spectrum. The "reversal" of the *D* lines of sodium is a familiar laboratory or lecture demonstration.

R. W. Wood showed[1] many years ago that a bulb containing sodium vapor at very low pressure would, when irradiated by light from an intense sodium flame, emit the *D* lines, and those only. To this phenomenon Wood gave the name *resonance radiation.*

The resonance is very sharp. An examination of the reemitted *D* lines showed that they were very narrow, their width corresponding almost exactly to the width predicted by the Doppler effect at the temperature of the sodium vapor. The width of the lines of the exciting source was much greater, since the tem-

[1] See Wood, R. W.: "Physical Optics." This book gives an account of these beautiful experiments on resonance radiation.

perature of the source was much higher than that of the vapor. On analyzing the light which had passed through the vapor, it was found that there was a narrow absorption line at the centers of the broad D lines. So far, the classical theory seems to agree with experiment.

But (the present) Lord Rayleigh showed[1] that if sodium vapor be illuminated by the *second* line of the principal series, $\lambda = 3{,}303$ Ångströms, both that line and the D line were emitted by the vapor. This fact cannot be explained by any application of the principle of overtones, since the frequency of the second line of the principal series bears no simple relation to the first line, the ratio of frequencies being $\frac{30{,}272}{16{,}973} = 1.7784$.

The quantum theory offers a simple explanation to observations such as those of Wood and of Rayleigh. The sodium atom in the vapor is in the *normal* state. To raise the atom from this normal state to an excited state, the return from which (to normal) emits the D lines, requires that the atom must be given energy *exactly* equal to $h\nu_D$, where ν_D is the frequency of the D line. The quantum energy of the incident D lines is exactly equal to this, and hence the sodium atom is *excited* by the absorption of this quantum. This explains Wood's observations. To excite the *second* line of the principal series, $\lambda = 3{,}303$ Ångströms, requires that the atom should be raised to an excited state higher than normal by exactly a quantum corresponding to $\lambda = 3{,}303$ Ångströms. When once in this latter excited state, the atom could return to the normal level, emitting the line $\lambda = 3{,}303$, or it could return to the intermediate level next above normal and by dropping from there to normal would emit the D lines. Absorption of the quantum corresponding to $\lambda = 3{,}303$ Ångströms, therefore, should result in the emission both of that line and of the D line, exactly as found by Rayleigh.

By following the same line of reasoning as that employed in considering excitation by electron impact, we see why it is that the *normal* sodium atom does not exhibit the phenomena of resonance radiation and absorption when radiated by some such line as, say, the second line of the sharp series, $\lambda = 6{,}161$ Ångstroms. The quantum energy corresponding to this line is not sufficient to raise the *normal* atom from its energy level even to

[1] STRUTT, R. J.: Bakerian Lecture, *Proc. Roy. Soc.*, vol. 96, p. 272 (1916).

the first level above normal which, as we have seen, requires a quantum corresponding to the D lines, $\lambda = 5{,}896$ and $5{,}890$ Ångströms.

Excitation by the absorption of quanta, therefore, is quite analogous to excitation by electron impact except for this one very important difference. The atom may become excited when colliding with an electron the energy of which *equals or exceeds* that required for the increase in energy-level; while *resonance* excitation takes place only when the energy of the incident quantum is *exactly equal to* that required to produce the particular change of state.[1]

(*d*) *Excitation by Collision with Other Atoms.*—The atoms of a gas are continually interchanging energy by collisions resulting from thermal agitation. We have seen in Chap. VIII that the mean energy of thermal agitation of a monatomic gas molecule at 300°C. is of the order of 0.078×10^{-12} ergs (*i.e.*, $\frac{3}{2}kT$). This we see is only a fraction of the energy, 3.33×10^{-12} ergs (page 386) required to raise the normal sodium atom from its normal state to the next higher energy level. Very rarely could it happen that a molecule of sodium vapor at room temperature would, as a result of a collision with another molecule, acquire sufficient energy to excite it. If, however, the temperature is raised, as by putting sodium in the Bunsen flame, the average kinetic energy of translation may become comparable with 3.33×10^{-12} ergs; collisions *between atoms* may then result in raising an atom to an excited state, and radiation may result. With further increases in temperature the higher members of the principal series, and also members of other series should appear. This is confirmed by experiment.

There is ample evidence to confirm the view that an atom A in an excited state may lose its energy of excitation by collision with another atom B, the *potential* energy of A being transferred to B. This potential energy may appear in B either (1) as energy of excitation, in which case B may later radiate its own characteris-

[1] If the energy $h\nu$ of the incident quantum equals (or *slightly* exceeds) the energy E_i required to remove the electron from the atom, the quantum may be absorbed, and ionization of the atom results. Data on this point are not very extensive. See MOHLER, FOOTE, and CHENAULT: *Phys. Rev.*, vol. 27, p. 37 (January, 1926); FOOTE, *Phys. Rev.*, vol. 29, p. 609 (1927).

tic frequencies; or (2), the *kinetic* energy of B may be increased, in which case A, initially excited, has returned to a lower, perhaps the normal, state *with no emission of radiation.* The latter kind of collision, in which the potential energy of an atom in the excited state appears as kinetic energy after collision, is known as a *collision of the second kind*—a very unsatisfactory name, since the name is not at all descriptive of the phenomenon.

As illustrative of these phenomena involving the transfer of the potential energy of an excited state from one atom to another may be mentioned the experiments on mercury vapor[1] which is excited to resonance radiation by the absorption of its own line $\lambda = 2{,}536$ Ångströms (equivalent to about 4.9 volts). If with the mercury vapor be mixed the vapor of thallium, the characteristic lines of the latter element appear *in addition to the mercury resonance radiation* when the mixture is radiated by the *mercury* line $\lambda = 2{,}563$, the mercury resonance radiation being then *weaker than when no thallium is present.* The thallium vapor *alone* is not excited to resonance by the mercury line. The phenomenon is explained by assuming that the mercury atoms are first raised to an excited state by resonance absorption of the line $\lambda = 2{,}536$; some of these excited atoms by collision with thallium atoms transfer this potential energy of excitation to the latter, which, then being excited, radiate their characteristic lines by returning to the normal state. The thallium lines so produced correspond to energy transfers in the thallium atom *less* than 4.9 volts.

Cario showed that the presence of argon in mercury vapor very materially reduces the intensity of the resonance radiation of the mercury vapor without, however, exciting argon radiation when the mixture is radiated by the $\lambda = 2{,}536$ line, although an examination of the light transmitted through the mixture shows that there is no diminution in *absorption* as a result of the presence of the argon. This effect is explained by assuming that collisions of the second kind take place between the excited mercury atoms and the argon atoms and that the *potential energy* of the former is transferred to *kinetic energy* of the latter.

(*e*) *Electrical Methods of Observing the Excitation of Atoms.*—Referring to Fig. 98, it is readily seen that if the potential difference between grid and filament be sufficiently high, the electrons

[1] LORIA, S.: *Phys. Rev.*, vol. 26, p. 573 (1925); CARIO, G.: *Zeit. für Physik*, vol. 10, p. 185 (1922); and CARIO and FRANCK, *Zeit. für Physik*, vol. 17, p. 202 (1923).

may be given sufficient energy to ionize by collision the molecules of the vapor in the space between the cylinder and the grid. In Fig. 99, the filament F is so connected to the battery B_2 that the potential difference between F and the grid S is less than, and in the opposite direction to, the potential difference between CC and S. Electrons accelerated from F toward S can therefore not reach CC. The cylinder CC is connected to earth through the sensitive electrometer E and the grounding key k. So long as no positive ions are produced in the space between S and CC, the cylinder should acquire no charge. But when the velocity of the electrons accelerated from F to S becomes sufficient to ionize the vapor, the positive ions should be attracted to CC and a so-called *ionization* current should be set up which is measurable by the rate at which the electrometer acquires a charge when the grounding key is open.

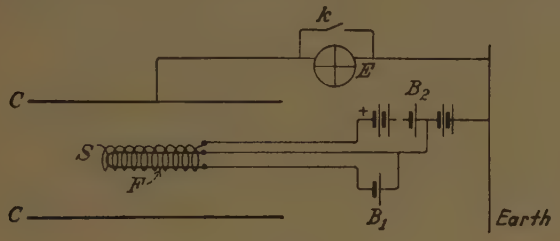


FIG. 99.

An effect of exactly this kind was observed by Lenard many years ago. He found that with such gases as air, hydrogen and CO_2, a current which he thought to be a true ionization current, began to flow when the exciting electrons had fallen through a potential difference of some eleven volts.

We have seen however from the experiments of Meggers, Foote and Mohler, that in the case of sodium vapor resonance radiation is produced by 2.09-volt electrons; and in the case of mercury vapor by 4.3-volt electrons. This resonance radiation, proceeding in all directions, falls on the inside walls of the cylinder, and, if the radiation be of sufficiently short wave length, *photoelectrons* will be expelled from the cylinder. Because of the direction of the field between CC and S these photoelectrons will flow toward the grid and we shall have in the circuit CB_2S a *photoelectric* current in exactly the same direction as if there were an ionization current due to the ionization of the vapor. This

"false" ionization current will begin abruptly as soon as the resonance potential is reached.

To separate the true ionization current from the photoelectric current Davis and Goucher[1] introduced a coarse wire gauze G surrounding the grid and just inside the plate *CC*. By means of a battery B_3,[2] (Fig. 100), this gauze may be maintained at either a positive or a negative potential with respect to *CC*, or *G* may be connected directly to *CC* without a battery. When *G* is sufficiently negative with respect to *CC*, photoelectrons, even if ejected from *CC* by the action of resonance radiation, will not reach *G*. Photoelectrons if ejected from *G*, however may reach *CC* and a photoelectric current may result. If now B_3 be reversed, so that *G* is positive with respect to *CC*, a photoelectric current in the opposite

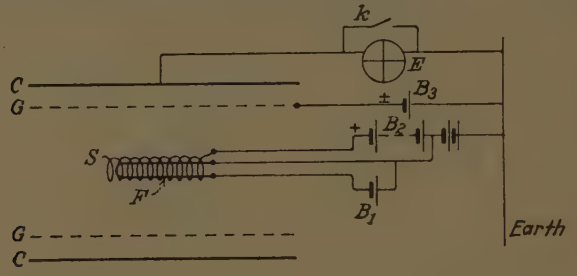


FIG. 100.—The apparatus of Davis and Goucher for studying ionization potentials.

direction should result. In either case the potential difference between *CC* and *G* is small compared to that between *G* and *S*. The true ionization current cannot be reversed by reversing the direction of B_3, since the positive ions produced between *S* and *G* acquire sufficient velocity so that, passing through the gauze, they will reach *CC* in spite of any small opposing field between *CC* and *G*.

With this type of apparatus Davis and Goucher obtained, for mercury vapor, curves of the type shown in Fig. 101, in which the abscissæ are the accelerating potentials between filament and grid, and the ordinates are the currents to the cylinder *CC* as measured by the rate of charge of the electrometer. Curve *A* was obtained when the gauze *G* was *positive* with respect to the

[1] *Phys. Rev.*, vol. 10, p. 101 (1917).

[2] Of course, these "batteries" are really variable potentiometric sources of *pd*.

cylinder; curve B when the gauze was *negative*. No current was observed until the accelerating voltage reached 4.9 volts. Beyond that voltage a current was observed (a to c in curve B, negative charging of cylinder; a to c' in curve A, positive charging of cylinder), *which could be reversed by reversing the battery* B_3, indicating that the current was a photoelectric current. At point c corresponding to 10.3 volts a sudden reversal of the direction of change of current took place, indicating that the

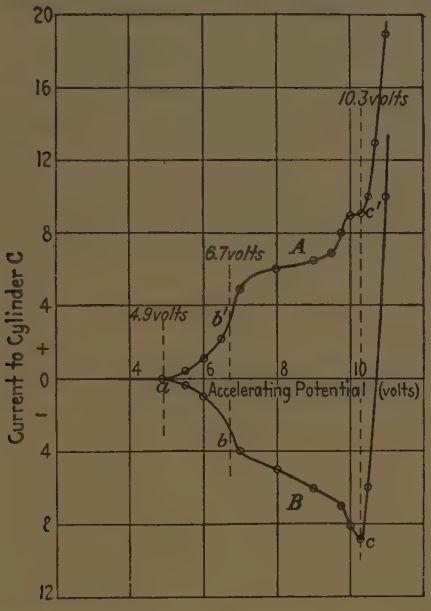


FIG. 101.—The resonance and ionization potentials of mercury vapor, as observed by Davis and Goucher.

cylinder was beginning to collect positive ions. Up to point c, curve A is qualitatively the mirror image of curve B.

The beginning of the photoelectric current at 4.9 volts is due to the excitation by electron impacts of the mercury line $\lambda = 2{,}536$, which then acts photoelectrically on the cylinder and the gauze. When the cylinder is positive with respect to the gauze, the photoelectrons move from gauze to cylinder; and *vice versa*. The rapid increase in photoelectric current which occurs when the voltage reaches 6.7 volts is attributed to the generation, at that voltage, of the mercury line $\lambda = 1{,}849$; while the sudden break in both curves at 10.3 volts is indicative of the beginning of the

real ionization current. 4.9 volts and 6.7 volts are spoken of as the *resonance potentials* of mercury vapor, and 10.3 volts is its ionization potential.

Many beautiful experiments have been devised to extend the data and theories regarding the excitation of atoms by impact or resonance. The reader will find further study in this field, from original sources, very fascinating. The literature is extensive.

13. Energy-level Diagrams. (*a*) *Hydrogen.*—We have seen that spectral lines originate when an atom changes from one state to another of lower energy. In Fig. 92 these states were represented pictorially in terms of Bohr's privileged orbits. Much more fundamental than this geometrical concept of the various states is the energy associated therewith. We can compute the energy of the atom in its various states from the known value of the spectral *terms*, the differences between which give the spectral lines. From these values of the energy, we can show by a diagram, known as the energy-level diagram or as the diagram of the stationary states, the origin of the various spectral lines and their interrelations, in a manner which is quite independent of any theory of atomic structure or of the mechanism of radiation, but which is, however, suggested by the geometrical diagram of Fig. 92. We shall illustrate the construction of the energy-level diagram by considering in turn the stationary states of hydrogen and of sodium.

Table VIII shows the first four lines in each of the four series in the spectrum of hydrogen, column one giving the wave length and column two the wave number. In column three are given, in wave numbers, the term values, the differences between which give the wave numbers of the lines. The first term value for each series is the convergence wave number for that series. The last column gives the quantum number of the term.

In these series of the hydrogen spectrum there are of course many repetitions of term values, the table containing only *eight different* terms. The wave numbers given for these terms are proportional to the energy values of the several states. We can, if we wish, compute the energy in, say, ergs by multiplying each term value in wave numbers by ch, *i.e.*, (see equation (23) Chap. IX).

$$W = chn$$

where c is the velocity of light, h is Planck's constant and n is the wave-number value of the term; or we may represent the

TABLE VIII.—TERM VALUES OF THE STATIONARY STATES OF THE HYDROGEN ATOM

λ, Ångströms	n, centimeters^{-1}	Terms, centimeters^{-1}	Quantum number, τ
	Lyman series		
		109,678	1
1,216.0	82,258	27,420	2
1,025.8	97,481	12,186	3
972.5	102,823	6,855	4
949.5	105,291	4,387	5
	Balmer series		
		27,420	2
6,562.8	15,233	12,186	3
4,861.3	20,565	6,855	4
4,340.5	23,032	4,387	5
4,101.7	24,373	3,047	6
	Paschen series		
		12,186	3
18,756	5,331	6,855	4
12,821	7,799	4,387	5
10,939	9,139	3,047	6
10,052	9,948	2,238	7
	Brackett series		
		6,855	4
4.05μ	2,468	4,387	5
2.63	3,808	3,047	6
2.16	4,617	2,238	7
1.94	5,141	1,714	8

energy of a particular state by its term value in wave numbers. It is convenient to treat the energy values of the various states as negative quantities, so that the state which has the highest *numerical* term value (the state $\tau = 1$ in hydrogen) has the lowest energy. In Bohr's theory this is equivalent to assuming that the energy of the atom is zero when the electron is at infinity.

We now arrange these eight terms in a table in order of descending energy values. This arrangement is shown in Table IX, in which, for comparison, is also shown the energy in ergs.

TABLE IX.—ENERGY VALUES OF THE STATES OF THE HYDROGEN ATOM ARRANGED IN DESCENDING ORDER OF MAGNITUDE

State	Energy in		Logarithm n
	Wave-number units, n	Ergs	
$\tau = 8$	− 1,714	-3.37×10^{-13}	3.234
7	− 2,238	− 4.39	3.350
6	− 3,047	− 5.99	3.484
5	− 4,387	− 8.61	3.642
4	− 6,855	− 13.45	3.836
3	− 12,186	− 24.0	4.086
2	− 27,420	− 53.9	4.438
1	−109,678	−215.5	5.040

The relative values of these states, or of these *levels of energy*, are shown by the horizontal lines in Fig. 102. (To secure a more open scale at the top, logarithms of wave numbers are plotted.) The transitions which give rise to the several lines are represented in an obvious manner by the arrows. The diagram brings out clearly the fact that each series "ends" on a particular energy level.

Actually, as we have seen in the discussion of the fine structure of the hydrogen lines, each of these levels has a "fine structure." Thus the level $\tau = 2$, is double (one energy value for the ellipse and one for the circle); the level $\tau = 3$ is triple, etc. These different levels for any given value of τ are too close together to be shown to scale on the diagram. The multiple character of the three levels $\tau = 2$, 3, 4 is shown diagrammatically by the light lines. And we recall (see p. 382) that the line H_α should be a triplet, according to the selection principle.

(*b*) *Sodium.*—By an exactly analogous procedure we construct the energy level diagram for sodium. We first form a table showing the term values, the differences between which give the wave numbers of the lines for the various series. These data[1] are shown in Table X. The arrangement is identical with that of

[1] Taken from Fowler's Report.

Table VIII for hydrogen, except as to the designation of the terms, which follows that used in the spectral series formulæ discussed in Chap. IX. These sodium series are in reality doublets (hence the Greek letters). To avoid confusion we omit this feature of the series, and consider them as singlet terms.

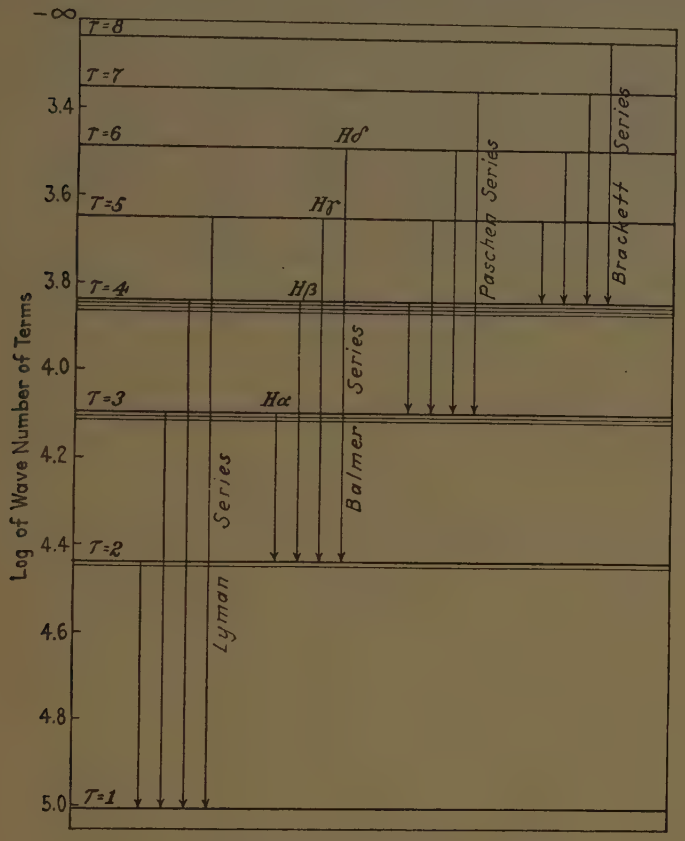


FIG. 102.—Energy-level diagram for the hydrogen atom.

We now sort out these terms and arrange them in a descending series of energy values, just as we did in the case of hydrogen. We note that there are four kinds of terms: σ, π, δ, and ϕ terms. We arrange like terms in vertical columns. The order of the columns is determined by the highest wave-number value (*i.e.*, *lowest* energy value) in the column, the σ column thus being first and the ϕ column last. We then have Table XI.

TABLE X.—TERM VALUES OF THE STATIONARY STATES OF SODIUM

λ, Ångströms	n, centimeters^{-1}	Terms, centimeters^{-1}	Term symbol
Principal series: $1\sigma - m\pi$			
		41,449	1σ
5,890.0	16,973	24,476	1π
3,302.3	30,273	11,176	2π
2,852.8	35,043	6,406	3π
2,680.3	37,298	4,153	4π
Diffuse series: $1\pi - m\delta$			
		24,476	1π
8,194.8	12,199	12,276	2δ
5,688.2	17,575	6,900	3δ
4,982.9	20,063	4,412	4δ
4,668.6	21,414	3,062	5δ
Sharp series: $1\pi - m\sigma$			
		24,476	1π
11,404	8,766	15,710	2σ
6,161	16,227	8,248	3σ
5,154	19,398	5,077	4σ
4,752	21,038	3,437	5σ
Fundamental: $2\delta - 3\phi$			
		12,276	2δ
18,459	5,416	6,860	3ϕ
12,678	7,886	4,390	4ϕ
		3,041	5ϕ

It will be observed that the wave numbers of the lines of a given spectral series are obtained by taking the differences between terms in *adjacent* columns: for example, $1\sigma - 2\pi$ gives the second line of the principal series; or $1\pi - 4\delta$ gives the third line of the diffuse series. This limitation of combinations to adjacent columns is suggestive, though perhaps vaguely, of the selection principle enunciated in Sec. 9, according to which the azimuthal quantum number of a given state can charge by only ± 1 in any transition between states which involves the emission of radiation. If we assign to the columns from left to right, beginning with the σ column as 1, a number k as shown (note

that the columns are arranged from left to right in ascending algebraic order of the *lowest* term in the column), the observed limitation of inter-state transfers to those in adjacent columns takes the form: $\Delta k = \pm 1$. The numeral k is identified with the *azimuthal* quantum number which we have previously called

TABLE XI.—ENERGY VALUES OF THE STATES OF THE SODIUM ATOM ARRANGED IN DESCENDING ORDER OF MAGNITUDE

Term symbol	Wave number, n, centimeters^{-1}				Energy (ergs)	Logarithm n
	σ terms	π terms	δ terms	ϕ terms		
5π	.....	2,907	.....	.....	5.71×10^{-13}	3.463
5ϕ	.....	.....	.....	3,041	5.98	3.483
5δ	.....	.....	3,062	.....	6.02	3.486
5σ	3,437	.....	.....	.....	6.75	3.536
4π	.....	4,153	.....	.....	8.16	3.618
4ϕ	.....	.....	.....	4,390	8.63	3.643
4δ	.....	.....	4,412	.....	8.67	3.645
4σ	5,077	.....	.....	.....	9.98	3.706
3π	.....	6,406	.....	.....	12.60	3.807
3ϕ	.....	.....	.....	6,860	13.48	3.836
3δ	.....	.....	6,900	.....	13.55	3.839
3σ	8,248	.....	.....	.....	16.20	3.916
2π	.....	11,176	.....	.....	21.9	4.048
2δ	.....	.....	12,276	.....	24.1	4.089
2σ	15,710	.....	.....	.....	30.9	4.196
1π	.....	24,476	.....	.....	48.2	4.389
1σ	41,449	.....	.....	.....	81.5	4.617
.....	$k = 1$	$k = 2$	$k = 3$	$k = 4$		

τ_ϕ, and the statement $\Delta k = \pm 1$ is identical with the selection principle previously stated.

The horizontal lines in Fig. 103 show in relative positions the energy levels for the sodium atom plotted to a logarithmic scale. The transitions giving rise to the several lines are shown by the arrows.

(*c*) Energy level diagrams of this kind are of great assistance in understanding and interpreting the interrelations among spectral lines. The reader will find it very instructive to prepare such a diagram starting with the spectral series data of, say,

potassium and including in the diagram the doublet levels and the resulting lines.

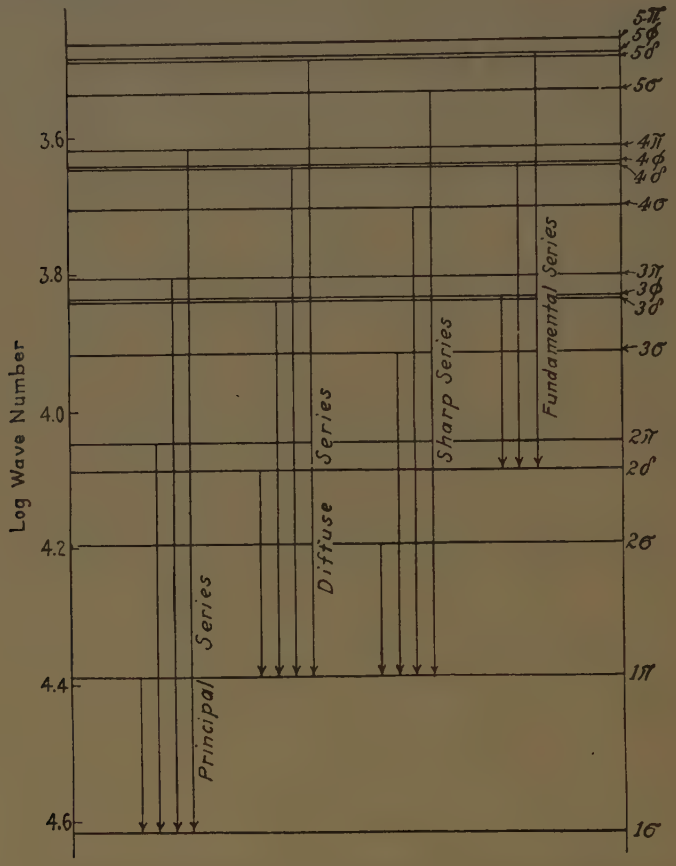


FIG. 103.—Energy-level diagram for the sodium atom, showing the origin of the several series of lines.

14. Notation; Inner Quantum Numbers.—A word about the notation for designating spectral terms: We have deliberately retained the simple notation of Fowler, as introduced in Chap. IX. This notation is easy to understand and is, therefore, preferable for a brief survey. The student who goes more deeply into the subject can familiarize himself with the particular notation which happens to be prevalent at the time! The essential *facts* are not changed by the notation in use. Notation depends on theory and the interpretation of the facts.

The need for a more comprehensive notation than Fowler's, as given in Chap. IX, can be illustrated by reference to Table XI. The term 3π (6,406) is a doublet. In the Fowler notation, the two terms of this doublet are indicated by subscripts, thus: $3\pi_1$ and $3\pi_2$. In general, many such "multiplicities" are found in spectra. In the spectrum of magnesium, as previously mentioned, are found two complete groups of terms—singlets and triplets. In Fowler's notation, we have represented the singlet terms by capital letters (S, P, D, and F) and the triplet terms by lower-case letters (s, p, d, and f) with subscripts 1, 2, and 3. Actually, however, the *s term* of the triplet series is a *singlet term*, while *p*, *d*, and *f* terms are *triplets*. The triplet nature of the *lines* of the spectrum results from the fact that the lines arise from the combination of the *terms*. Thus, the principal series $p(m) = 1s - mp$ arises from combinations of the $1s$ *term* with each in turn, of the three *p terms*. The sharp series $s(m) = 1p - ms$ arises from combinations of each of the three *p terms* with the singlet *s term*. Thus, the components $s_1(1)$, $s_2(1)$, and $s_3(1)$ of the first "line" in the sharp (triplet) series of calcium are given by the following combinations:

$$s_1(1) = 1p_1 - 1s = 33{,}989 - 17{,}765 = 16{,}226$$
$$s_2(1) = 1p_2 - 1s = 34{,}095 - 17{,}765 = 16{,}330$$
$$s_3(1) = 1p_3 - 1s = 34{,}147 - 17{,}765 = 16{,}382$$

Since, therefore, the *s* terms are single and the *p* terms are triple, we should expect the sharp series of lines and the principal series of lines to consist of triplets, as is actually observed to be the case.

The diffuse series, however, arises from combinations of the *p* terms with the *d* terms, thus: $d(m) = 1p - md$. Since, in calcium, both the *p* terms and the *d* terms are triple, we might expect the *lines* of the diffuse series to consist of *nine* components, instead of three. Actually, including the satellites mentioned on page 311, the diffuse series of lines in calcium contains *six* components, which we tabulate in Table XII. In this table, the wave numbers of the *p* terms are written above the vertical columns, the designation of the terms in the Fowler notation being written *above* the wave number. Similarly, the wave numbers of the *d* terms are written at the left of the horizontal rows. The wave numbers (observed) of the six components, together with the combinations of terms which give rise to the

TABLE XII.—COMPONENTS OF THE FIRST "LINE" IN THE DIFFUSE (TRIPLET) SERIES OF CALCIUM

Terms→ ↓	$1p_1$ 33,988.7 cm.$^{-1}$ 1^3P_2	$1p_2$ 34,094.6 cm.$^{-1}$ 1^3P_1	$1p_3$ ←old notation 34,146.9 cm.$^{-1}$ 1^3P_0 ←new notation
$1d_3$ 28,968.8 cm.$^{-1}$ 1^3D_1	$1p_1 - 1d_3$ 5,019.6 $1^3P_2 - 1^3D_1$	$1p_2 - 1d_3$ 5,125.2 $1^3P_1 - 1^3D_1$	$1p_3 - 1d_3$ 5,177.3 $1^3P_0 - 1^3D_1$
$1d_2$ 28,955.2 cm.$^{-1}$ 1^3D_2	$1p_1 - 1d_2$ 5,032.9 $1^3P_2 - 1^3D_2$	$1p_2 - 1d_2$ 5,139.5 $1^3P_1 - 1^3D_2$	$1p_3 - 1d_2$ missing $1^3P_0 - 1^3D_2$
$1d_1$ 28,933.5 cm.$^{-1}$ 1^3D_3	$1p_1 - 1d_1$ 5,055.1 $1^3P_2 - 1^3D_3$	$1p_2 - 1d_1$ missing $1^3P_1 - 1^3D_3$	$1p_3 - 1d_1$ missing $1^3P_0 - 1^3D_3$

components, are given in the squares. It is observed that the three components are missing corresponding to the combinations $1p_2 - 1d_1$; $1p_3 - 1d_2$; and $1p_3 - 1d_1$. There is evidently in operation here a selection principle somewhat similar to that discussed in connection with the fine structure of the hydrogen lines. We shall return to this point presently.

Multiplicities much higher than triplet terms occur in spectra. Indeed, multiplicities as high as octets have been found. These multiplicities exhibit a beautiful regularity not only among the several groups of terms of the spectrum of a given element but also, as we shall mention in Chap. XI, from element to element in the periodic table of the elements. In a singlet system of terms—as in the singlet system of calcium—all the terms are singlets. In a doublet system, the S terms[1] are singlets and the P, D, F . . . terms are doublets. In a triplet system, the S terms are singlets and the remainder are triplets. In a septet system, the S terms are singlets, the P terms are triplets, the D terms are quintets, and the F terms are septets. The multiplicity of a system of terms is designated by the *highest* multiplicity found in the system. The S terms are always singlets; the P terms are never more than triplets; and so on.

Table XIII shows the multiplicities of the terms (S, P, D . . .) of the several systems (singlets, doublets, triplets . . .).

[1] We here use the capital letters to designate terms, irrespective of multiplicity.

The P terms in a sextet system are triplets. The F terms in an octet system are septets; and so on

With this complexity of systems and of terms, it is obvious that designation of terms by capital letters, Greek letters and lower-case letters for singlet, doublet, and triplet systems, is

TABLE XIII.—SHOWING THE MULTIPLICITY OF TERMS IN SPECTRAL SYSTEMS

System→		Singlet	Doublet	Triplet	Quartet	Quintet	Sextet	Septet	Octet
Terms	k								
S	1	1	1	1	1	1	1	1	1
P	2	1	2	3	3	3	3	3	3
D	3	1	2	3	4	5	5	5	5
F	4	1	2	3	4	5	6	7	7
G	5	1	2	3	4	5	6	7	8

no longer adequate. Many alternative systems for the designation of terms have been proposed. The one most generally adopted is that proposed by Russell and Saunders[1] and referred to as the "new notation" in Table XII. In this notation, the capital letters S, P, D, F, G . . . are used for the sequences of terms. Since the azimuthal quantum numbers of these sequences are, respectively, 1, 2, 3, . . . , we may think of S, P, D . . . as not only designating a *sequence* but also as standing for 1, 2, 3 . . . , the *azimuthal* quantum number of that sequence. Instead of using different letters for the different multiplicities, as π for doublets, p for triplets, etc., Russell and Saunders prefix as a superscript to the letter a number, as ${}^2P$, to indicate the multiplicity of the *system* (*not* the term) to which the term belongs. Thus, ${}^2P$ refers to the P terms of a doublet system, ${}^5P$ refers to the P terms of a quintet system, etc.

To designate the several components of a sequence, *suitably chosen* subscripts are used. Thus, in a quintet system, the P terms have a threefold multiplicity— we require three subscripts. The D terms have a fivefold multiplicity—we require five subscripts. These subscripts are the so-called *inner quantum numbers*, symbol j (see below). Their selection, based on considerations partly empirical, partly theoretical, is by no means an arbitrary matter. Empirically, we may illustrate the choice

[1] *Astrophys. Jour.*, vol. 61, p. 64 (January, 1925).

of these inner quantum numbers (and, incidentally, the Russell-Saunders notation) by reference to Table XII. The three P terms, the first in the P sequences in the triplet system of calcium, are designated, respectively, by 1^3P_2, 1^3P_1, 1^3P_0, the subscripts 2, 1, 0 being the inner quantum numbers of these P terms. Likewise, the three D terms, which combine with these P terms to give the first "line" of the diffuse series, are represented by 1^3D_1, 1^3D_2, 1^3D_3, the inner quantum numbers here being 1, 2, 3. With this selection of inner quantum numbers ("mnemonic subscripts," one may prefer to call them) it is noted (see Table XII) that *only those combinations of terms take place for which the change in the inner quantum number is* ± 1 or 0. All other combinations are "ruled out;" *e.g.*, there is no component corresponding to $1^3P_1 - 1^3D_3$, since, for this combination, the change in j is $+2$.

Observations on more complex systems, quartets, sextets, etc., have led to a selection rule for this inner quantum number, which rule, *when the inner quantum number is properly chosen*, states that the permissible change Δj, in j, is given by

$$\Delta j = \pm 1 \text{ or } 0, \tag{85}$$

the change $\Delta j = 0$ for *zero* values of j being also ruled out. Table XIV gives the inner quantum numbers for the S, P, D . . . sequences of singlet, triplet, quintet, and septet systems, these numbers being so chosen that the selection rule (equation (85)) predicts correctly the component lines *actually observed* in the spectra, as shown in Table XII. Conversely, from the inner quantum numbers, as assigned in this table, together with the two selection rules (equations (84) and (85)) it is possible to

$$\Delta k = \pm 1$$
$$\Delta j = \pm 1 \text{ or } 0$$

predict the "permitted" combinations between terms.

TABLE XIV.—INNER QUANTUM NUMBERS, j

Sequence	Singlet system	Triplet system	Quintet system	Septet system
S ($k = 1$).....	0	1	2	3
P ($k = 2$).....	1	2 1 0	3 2 1	4 3 2
D ($k = 3$).....	2	3 2 1	4 3 2 1 0	5 4 3 2 1
F ($k = 4$).....	3	4 3 2	5 4 3 2 1	6 5 4 3 2 1 0
G ($k = 5$).....	4	5 4 3	6 5 4 3 2	7 6 5 4 3 2 1

On theoretical grounds, the inner quantum number is associated with the angular momentum of the atom as a whole; *i.e.*, the inner quantum number is determined by the vector sum of the angular momenta of the several electrons of the atom in their orbital motion about the nucleus. We shall say a word further about this in the next chapter. Mention may also be made of the fact that both theory and observation demand the use of half-quantum numbers, such as $j = \frac{1}{2}, \frac{3}{2} \ldots$ It will not be profitable for us to enter into a further discussion of this point.

15. Molecular Spectra.—In the preceding sections of this chapter, we have considered only those spectra which are emitted by the *atom* as a result of energy changes in the electron system surrounding the atom. We may think of this type of spectra as having its origin in a *periodic phenomenon* associated with the atom, namely, the *revolution* of the electrons around the atomic nuclei, although, according to the quantum theory, the emitted frequencies are not the same as the frequencies of these orbital motions but are determined by the quantum condition

$$h\nu = W_1 - W_2$$

The orbital motions of the electrons around nuclei constitute only one of several types of periodic phenomena which, on the basis of our present picture of molecular structure, should be exhibited by matter. We saw, in Sec. 10 of Chap. VIII, that the variation of the molecular heat of gases with temperature could be explained by assuming that, in addition to translation, the molecules of a polyatomic gas have degrees of freedom as regards both rotation and vibration. It may be expected that these types of periodic motions would also result in spectral phenomena and that to the energy changes associated with these motions we might apply the quantum laws introduced by Bohr. Such proves to be the case. In addition to the Balmer type of spectra discussed in Chap. IX there are found both emission and absorption lines comprising, in general, the type of spectra known as *band* spectra (see Chap. IX, Sec. 10). These can be definitely ascribed to changes in *molecular* energy, which may be thought of as made up of three parts: (1) rotational energy of the molecule, say a diatomic molecule, about an axis through its center of mass and at right angles to the line joining the two nuclei; (2) vibrational energy due to the relative vibratory motion of the two atoms with respect to each other; and (3) energy of the electronic system

associated with the molecule. Corresponding to each of these three types of energy there is a quantum number, m_r, m_v, and m_e, respectively, changes in which play the same role in band spectra as does the orbital quantum number in the Balmer type of spectra. For a full account of band spectra the reader is referred to "Molecular Spectra in Gases,"[1] by the Committee on Radiation in Gases of the National Research Council. In this section, we shall discuss only two simple cases illustrative of the fundamental concepts involved.

Consider the rotation of a dumb-bell-shaped (*i.e.*, diatomic) gaseous molecule about an axis passing through its center of mass and perpendicular to the line joining the two nuclei. Let the moment of inertia of the molecule about this axis be I, assumed constant and independent of the angular velocity ω. The angular momentum M is given by

$$M = I\omega \tag{86}$$

and the rotational kinetic energy T is

$$T = \tfrac{1}{2}I\omega^2 \tag{87}$$

Let it be assumed that we can apply to this angular momentum Bohr's quantum condition (equation (18))

$$\oint p dq = \tau h$$

Inserting in this general equation the angular momentum M and the corresponding angular coordinate θ, we have, for the rotating molecule,

$$\oint M d\theta = 2\pi M = m_r h \tag{88}$$

where m_r, which replaces τ, is the molecular rotational quantum number. Eliminating M and ω from equations (86), (87), and (88) gives

$$T = \frac{h^2}{8\pi^2 I} m_r^2 \tag{89}$$

This is the kinetic energy of the rotating molecule for a given quantum "state of rotation" designated by the integer m_r. Applying Bohr's quantum condition (equation (31)), when the

[1] *Nat. Research Council, Bull.* 57 (December, 1926).

energy changes from T_1 corresponding to $m_{r,1}$ to T_2 corresponding to $m_{r,2}$, a quantum of energy $h\nu$ is emitted, given by

$$h\nu = T_1 - T_2 = \frac{h^2}{8\pi^2 I}(m_{r,1}^2 - m_{r,2}^2) \qquad 90)$$

from which we obtain, for the frequency ν,

$$\nu = \frac{h}{8\pi^2 I}(m_{r,1}^2 - m_{r,2}^2) \qquad (91)$$

Now, since the momentum M involves only angular motion, we may regard the quantum number m_r as similar to the azimuthal quantum number k for electron orbits, which, according to equation (84), may change by only ± 1. We may, therefore, apply to m_r the selection rule for azimuthal quantum numbers,

$$\Delta m_r = \pm 1$$

from which we see that *i.e.* $m_{r,1}$ can differ from $m_{r,2}$ in equation (91) by only 1 unit. For the *emission* of radiation, therefore,

$$m_{r,2} + 1 = m_{r,1},$$

and, dropping the subscripts, equation (91) becomes

$$\nu = \frac{h}{8\pi^2 I}(2m_r + 1) \qquad (92)$$

This equation predicts a series of lines which, for the several integer values of m_r, should occur at constant frequency intervals $\Delta\nu$ given by

$$\Delta\nu = \frac{h}{4\pi^2 I} \qquad (93)$$

Such a spectrum is called a *pure rotation spectrum.*

From a knowledge of the approximate value of the moment of inertia I of molecules (of the order of 10^{-40} gram. cm.^{2}), these "rotation" lines should be in the far infra-red. Czerny[1] finds in the absorption spectrum of HCl a group of lines in the neighborhood of 50 to 100μ, the frequencies of which are given by the relation

$$\nu = (20.8 \times c)m \qquad (94)$$

where c is the velocity of light and m stands for successive integers. Comparing this empirical result with equation (93),

[1] *Zeit. Physik*, vol. 34, p. 227 (1925).

we see that the *difference* in frequency $\Delta\nu$ between successive lines should be

$$\Delta\nu = \frac{h}{4\pi^2 I} = 20.8 \times c$$

From this, one computes that the moment of inertia I of the HCl molecule is 2.7×10^{-40} gram. cm.^{2}—which corresponds to a distance apart of the two atoms of HCl of, approximately, 1.2×10^{-8} cm., a result which is certainly of the correct order of magnitude.

In general, a diatomic molecule may rotate and vibrate at the same time. Its total energy is then partly rotational, partly vibrational, with the latter of which is associated a quantum number m_v analogous to m_r for rotation. Any given change of state may involve simultaneous changes in both the quantum numbers m_r and m_v—in somewhat the same way as the elliptical electronic orbits involve changes in both azimuthal and radial quantum numbers. That is to say, the energy $h\nu$ of a given emitted quantum may come partly from the rotational energy, partly from the vibrational energy of the molecule. In that event, it can be shown[1] that the frequency should be given by an equation of the form

$$\nu = \nu_v + \frac{h}{8\pi^2 I}(\pm 2m_r + 1) \qquad (95)$$

where ν_v is the contribution to the frequency ν due to the vibration and the second term on the right is the contribution due to rotation. It turns out that ν_v is, in general, much the larger of the two terms. For a given ν_v, the second term has a *series* of values for the several integer values of m_r. (That is, associated with a given quantum jump in vibratory energy there may be any one of a large number of jumps in rotational energy.) Equation (95), therefore, predicts a series of lines differing from each other by frequency differences $\Delta\nu$ given by

$$\Delta\nu = \frac{h}{4\pi^2 I}$$

the same as for jumps involving rotational energy only, but coming at *higher* frequencies. This type of spectrum is known as a *rotation-vibration* spectrum. Spectra of this type occur in the near infra-red. For example, in the absorption spectrum of HCl occurs a series of equally spaced bands, or lines, in the

[1] See *Nat. Res. Council, Bull.* 57, *loc. cit.*

neighborhood of 3.6μ, the frequency separation of which agrees with that computed from the pure rotation spectrum of HCl.

A still further complication results when changes of energy of the molecular electron system is superimposed on the rotation-vibration energy changes. This produces the so-called *electronic* band spectra—of which the cyanogen bands referred to in Chap. IX, Sec. 10, are examples.

The solution, even though still incomplete, of the very complex problem of molecular spectra is one of the most astonishing successes of the quantum theory.

CHAPTER XI

THE ARRANGEMENT OF ELECTRONS IN ATOMS

The Rutherford-Bohr atom *model* was built out of raw material which grew in the field of physics. The atom *itself*, originally a child of Chemistry, was soon adopted by physics and has long claimed this joint parentage. In all of our theories and theorizing, we must not fail to distinguish between the *real atom* and the *atom model*. The ultimate atom model—if such perfection be ever reached—must explain and agree with the facts of chemistry, which facts are just as cogent as are the facts of physics. The task of constructing an *atom model* which shall do all the things that *atoms* are made to do by both chemists and physicists was (and is!) gigantic. A model, built and trained to act as marionette for a physicist, could not be expected to perform well for the chemist.

Out of the material furnished by chemistry have been built various atom models, which, in the main, go by the generic name of *static* atom models, as contrasted with a model of the Rutherford-Bohr type, which is a *dynamic* model. The origin of the two terms is significant. The dynamic model has been constructed by the physicist largely from information acquired in watching atoms *in action* or, at least, in watching the results of their activity, such as the emission of radiation, characteristic or black body, or the scattering of α particles, and the like. It is natural, therefore, that the physicist should picture an atom as full of *moving* mechanisms. His one static atom, the Thomson model, proved inadequate. The chemist, on the other hand, is somewhat more concerned with the atom at rest. He weighs it in finding what combinations it makes with other atoms; he observes it apparently at rest in crystals, except for possible thermal agitation; he thinks of it as occupying a definite position as one of the constituent atoms of various complex molecules, being held in place by certain interatomic forces, perhaps of electrostatic origin. It was difficult to see how a thing so full of whirling mechanisms as the physicist pictured the atom to be

could keep as quiet as the chemist found it when *he* looked at it. Hence, the static atom.

PART I. THE STATIC ATOM

1. The Inert Gases: Atomic Numbers and Properties.—The suggestion that the electrons of the nuclear atom occupy *fixed* positions in concentric shells was first made by G. N. Lewis[1] and was, in a sense, a revival of the Thomson atom, modified, as a result of Rutherford's experiments on the scattering of α particles, by putting the positive change, the nucleus, *inside* the concentric shells and at their center. This suggestion was greatly extended by Langmuir,[2] who discussed in detail the relation of this model to many chemical and physical properties of atoms and molecules. Mention was made, in the preceding chapter, of the origin of the concept of atomic number, a concept which was firmly established by Moseley (see Chap. XII). As a result of Moseley's work, the total number of elements up to and including uranium was fixed at 92, and the atomic number of each element was unambiguously assigned. The atomic numbers of the elements are shown in Appendices I(a) and I(b), the latter giving the elements as arranged in the well-known periodic table. Strictly speaking, the atomic number of an atom is the ratio of the (positive) charge on its nucleus to the (*numerical* value of the) charge on the electron. This ratio is numerically equal to the number of electrons which surround the nucleus of the atom in its *normal* condition.

Note.—When, as a result of the action of some physical agency, an atom loses 1 or more electrons, the atom is said to be *ionized*—singly ionized if it has lost 1 electron, doubly ionized if it has lost 2 electrons, etc. The loss of 1 electron leaves the atom with an excess of *positive* charge equal numerically to the charge on the electron. We may designate such an atom by writing "+" as a superscript (or subscript) following the chemical symbol of the atom. Thus, singly ionized magnesium is written Mg^{+}; doubly ionized, Mg^{++}. Or, Roman numerals may be used as subscripts; thus: Mg_{I}, Mg_{II}, . . . Mg_{VI}, etc.

All theories of the spatial distribution of the extranuclear[3] electrons in atoms start from the experimentally observed fact

[1] *Jour. Amer. Chem. Soc.*, vol. 38, p. 762 (1916).

[2] *Jour. Amer. Chem. Soc.*, vol. 41, p. 868 (1919); *Jour. Ind. Chem. Eng.* (April, 1920); *Nature*, vol. 105, p. 261 (April, 1920).

[3] "Extranuclear" since, as we shall see later, the nucleus contains electrons.

that as we proceed along the sequence of the elements from hydrogen to uranium we come *periodically* upon *monatomic* elements which form no chemical compounds with atoms of other elements. These elements are the so-called *inert gases*, helium, neon, argon, krypton, xenon, and niton. In addition to their chemical inactivity, these elements, as is shown by Table I, have very low melting and boiling points. If we make the very reasonable

TABLE I.—MELTING POINTS AND BOILING POINTS OF THE INERT GASES

Atomic number	Element	Melting point, degrees Centigrade	Boiling point, degrees Centigrade
2	He	<-272.2	-268.9
10	Ne	-248.7	-245.9
18	Ar	-189.2	-187.0
36	Kr	-169	-151.8
54	Xe	-140	-109.1
86	Nt	-71	
1	hydrogen	-259.1	-252.7

assumption that the chemical activity of an atom is conditioned somehow upon the magnitude of its external electric (or perhaps magnetic) field, which field would also determine the melting point and the boiling point, we conclude that the atoms of the inert gases have very weak external fields. Or, in different words, *the arrangements of the extranuclear electrons in the atoms of the inert gases, whatever that arrangement is, is such as to give to those atoms a very stable structure.* Now, when atoms combine with atoms of the same kind, or of other kinds, to form molecules, the electron systems of the several atoms unite to form some kind of spatial distribution of electrons characteristic of the molecule. All atom-model builders, whether chemists or physicists, make as a fundamental postulate—it amounts almost to an axiom—that *chemical combinations between atoms in forming molecules tend to take place in such a way as to imitate, by the combination, the arrangement of electrons in the atoms of the inert gases*—again, *whatever the latter arrangement may be.* The steps, then, in building up theories of the spatial distribution of electrons in atoms are (1) to make some sort of reasonable guess as to the distribution in the inert gases and then (2), guided, in part, by data on chemical combinations which atoms are observed to

make with each other and, in part, by spectroscopic data from the visible, the near-visible, and the X-ray regions of the spectrum, so to arrange the electrons in the other atoms as to be able to predict, from the proposed arrangement, the observed physical and chemical facts.

This "reasonable guess" concerning the arrangement of electrons in the atoms of the inert gases originally grew out of an observation by Rydberg,[1] made soon after Moseley's work had assigned atomic numbers to the elements, that the atomic numbers Z of the inert gases can be expressed by a simple numerical series, as follows:

$$Z = 2\,(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 \ldots) \qquad (1)$$

$\leftarrow$He$\rightarrow$
$\leftarrow\!\!-$Ne$-\!\!\rightarrow$
$\leftarrow\!\!-\!\!-$Ar$-\!\!-\!\!\rightarrow$
$\leftarrow\!\!-\!\!-\!\!-Kr-\!\!-\!\!-\!\!\rightarrow$
$\leftarrow\!\!-\!\!-\!\!-\!\!-Xe-\!\!-\!\!-\!\!-\!\!\rightarrow$
$\leftarrow\!\!-\!\!-\!\!-\!\!-\!\!-Nt-\!\!-\!\!-\!\!-\!\!-\!\!\rightarrow$

For example, the atomic number of argon is 18. And

$$18 = 2(1^2 + 2^2 + 2^2)$$

This numerical series suggests that the electrons in these inert gases may be arranged in "layers" or shells: that the argon atom, for instance, contains three shells, the first shell containing $2 \cdot 1^2$ electrons; the second, $2 \cdot 2^2$; and the third $2 \cdot 2^2$; and so on, for the other inert gases. The factor 2 suggests symmetry of some kind.

Of course, this suggestion that the electrons may be arranged in layers contains no hint as to the state of the electrons in those layers. The electrons may be in orbital motion around the nucleus, or they may be either at rest or in vibration about some fixed position of equilibrium determined by the force field of the nucleus. If we assume the latter, as is *apparently* demanded by the *static* atom of the chemist, we must invoke the aid of some *unknown* force or law of force to produce equilibrium, since, as we saw in discussing the problems of equilibrium raised by Rutherford's nuclear atom, electrons *outside* the nucleus cannot be in equilibrium under the action of the inverse-square law of electrostatic force, alone. If, however, with Bohr, we assume

[1] *Phil. Mag.*, vol. 28, p. 144 (1914).

the former, we must invoke the aid of some unknown law or principle which makes it possible for an electron to execute orbital motion and, in so doing, to evade the inexorable laws of the electromagnetic theory. Formally, there is nothing to choose between the two horns of the dilemma. It will be instructive, therefore, for the time being, to follow the Lewis-Langmuir concept of stationary electrons, in discussing the evolution of the atom model,[1] especially since, in the initial formulating of ideas, it is easier to visualize the *static* than the dynamic atom.

Helium has 2 electrons. Since its inertness indicates that the structure of the helium atom is stable, the general law is suggested that, in combination with a nucleus (or, perhaps, nuclei), 2 electrons tend to make a stable, a *very* stable, combination. Why, we cannot say, until we know much more about the force fields surrounding nuclei and electrons. We take the stability of such a *pair* of electrons as an empirical *fact.*

Neon has 10 electrons: $10 = 2(1^2 + 2^2)$. We may *guess* that, since 2 electrons make a very stable combination, (*a*) 2 of the 10 electrons in neon are, somehow(!), combined in a stable pair around the neon nucleus (charge + 10) and (*b*) the remaining 8 electrons (2×2^2) form an outside layer. Again, since the structure of neon is stable, it follows that, *whatever the reason*

[1] There has been much criticism of the "static" atom model. Thus, one eminent writer states: "It is true that if the eleven postulates, on which Langmuir's theory is founded, are granted, and a certain freedom of interpretation be allowed, a great body of chemical observation is covered by this theory, but it must be observed that the postulates have very much an *ad hoc* character, often paying little attention to any previously established laws of electromagnetism." As if Bohr's postulates or Planck's quantum hypothesis paid any attention to the "previously established laws of electromagnetism!" It is the essence of the whole quantum theory that "*ad hoc*" assumptions are made, *ad libitum*, where such assumptions serve a useful purpose. Of course, the fewer such assumptions the better. But, logically, we may as well make a dozen assumptions contravening classical theory, as one. If atom models growing out of the concept of the orbital motions of electrons, *i.e.*, the so-called "dynamic" atom models, *have* been more successful than static atom models, it is because the former have been more prolific in explaining and interpreting physical phenomena, rather than because of any superiority in fundamental tenets. The great number of *qualitative* deductions from static atom models, deductions in agreement with chemically observed facts, is very suggestive. But *the computation of spectral frequencies, even for* 1 *atom, from fundamental constants of nature is a quantitative achievement that is all but convincing.*

may be, a group of 8 electrons, inside which are (one or more) stable groups, tends to make a stable combination. Since we know of no reason why these 8 electrons should *not* be disposed symmetrically about the nucleus, it is natural to assume that they are located at the corners of a cube—although we must admit that this argument is much like that by which Pythagoras proved the world to be round: since the sphere is the most perfect figure! On account of this suggestion of the "cubical" arrangement of these 8 electrons, this picture of the atom is frequently referred to as the *cubical* atom. The group of 8 electrons is called an *octet*.

Argon has 18 electrons, $2(1^2 + 2^2 + 2^2)$. It is reasonable to picture the first 10 of these as occupying positions similar to those in the neon atom and the remaining 8 as forming another layer outside this neon-like structure. We shall designate the distribution of electrons in groups surrounding the nucleus by an obvious abbreviation which gives the number of electrons in successive layers: For helium, the distribution is (2); for neon, (2, 8); for argon, (2, 8, 8). Langmuir assumed that the electrons of this second group of 8 in argon form eight stable pairs with the first group of 8, and that these eight pairs occupy eight *cells* in a layer around the central pair and the nucleus. Bury,[1] on the contrary, subsequently showed that this latter assumption is unnecessary and that the properties of the elements could be more readily explained by the assumption that the *outside* stable group is *always* a group of 8 electrons. Before taking up the distribution of electrons in the atoms of the inert gases of higher atomic number than argon, we shall pause to consider the application, to chemical combinations of the lighter elements, of the following two general principles:

1. *Electrons around, or in combination with, nuclei tend to form either groups of* 2 (*pairs*) *or groups of* 8 (*octets*). (We shall have to extend this to groups of 18 and of 36 for the heavier atoms.)
2. *Such combinations of atoms to form molecules tend to take place as make it possible for the electron systems of the combining atoms to imitate so far as possible the configuration of the electrons in one or the other of the inert gases.*

[1] *Jour. Amer. Chem. Soc.*, vol. 43, p. 1602 (1921).

2. Some Chemical Properties of the Lighter Elements. (*a*) *Hydrogen* ($Z = 1$).—This element has 1 electron associated with a single-charged nucleus. Since we postulate that electrons tend to form pairs or octets, it may be expected that (atomic) hydrogen would be very active chemically either in combining its single electron with an electron from another atom to form a helium-like pair or in joining its electron with a group of electrons in another atom to assist in the completion of an octet. A pair could also be formed by the union of 1 hydrogen atom with another to form molecular hydrogen H_2. H_2 should be a helium-like structure (in so far as concerns the electrons) and should, therefore, resemble helium in its physical and chemical properties. Hydrogen has a very low boiling point (see Table I) and in its *molecular* state is comparatively inactive.

(*b*) *Helium* ($Z = 2$).—Of course, we cannot *explain* the properties of helium, since those properties are taken as a standard of comparison (more correctly, of *imitation*).

(*c*) *Lithium* ($Z = 3$).—We may expect 2 of the 3 electrons of lithium to form a stable pair around the $+3e$ nucleus, the combination (nucleus plus 2 electrons) being called the *kernel* of the atom. This kernel has a net *unit* (*i.e.*, $+e$) positive charge. The other electron is positioned at a greater distance from the kernel. The distribution of the electrons in lithium is (2, 1). On account of this distribution of charge, the lithium atom should have an electric moment, and, accordingly, lithium atoms should "line up" like iron filings in a magnetic field, as is shown diagrammatically in Fig. 104(*a*), where the dots represent electrons, each with a negative charge $-e$; and the circles, the lithium nuclei with their threefold positive charge $+3e$, close to which are the 2 electrons which make the stable pair, the combination $(+3 - 2)e$ giving to the *kernel* a *net* charge $+e$. This lattice array of lithium atoms, of course built up in three dimensions, constitutes a *crystal*, in which are numerous comparatively *free* electrons. Lithium then, should be a *crystalline* solid and should be a *good conductor* of electricity. Lithium *is* a crystalline, conducting (metallic) solid with a melting point at 186°C.—much higher than the melting points of hydrogen and helium, because of the greater electric force holding the constituent parts of the crystal, the *ions*, in place.

It is to be observed that in the crystal of lithium as shown in Fig. 104(*a*), there is no particular kernel and electron which we

can picture as belonging together to form *a molecule*, since each kernel is surrounded by a *number* of electrons, and *vice versa*. A crystal of this type is, therefore, composed of *ions* but not of *molecules*. Even in the liquid phase, the *ionic* condition persists. In the solid and the liquid phase, therefore, there are no lithium *molecules* as separate entities. Only in the vapor phase may we speak of "lithium molecules."

When a lithium atom and a hydrogen atom are brought together, the 4 electrons and the 2 nuclei combine in such a way

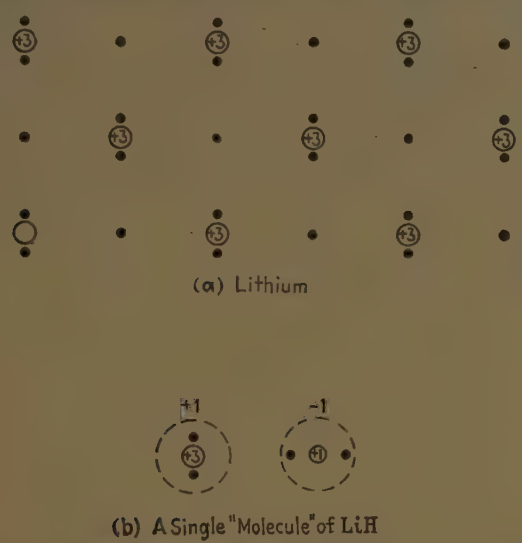


FIG. 104.—(*a*) Schematic representation of the crystalline structure of metallic lithium. The dots represent electrons. The circle is the positively charged lithium nucleus; (*b*) the molecule of lithium hydride, showing its ionic composition.

as to form *two* stable pairs of electrons, as is shown diagrammatically, in Fig. 104(*b*). The one group, A, has a net charge $+e$, and the other, B, a net charge $-e$. We should, therefore, predict the compound LiH. For the same reasons as in the case of metallic lithium, these combinations of pairs should build up into a three-dimensional crystalline lattice. Since there are now no *free* electrons, this crystal should be a poor conductor of electricity. The crystal LiH is known, and it has a high melting point (680°C.), which could be predicted from the comparatively strong forces between the ions. When melted however, LiH

should be made up of Li^+ and H^- *ions;* it should, therefore, be an *electrolytic* conductor—which agrees with the facts.

(*d*) *Fluorine* ($Z = 9$) *and Sodium* ($Z = 11$).—(We pass, for a moment, the intervening elements.) Between fluorine and sodium comes the stable inert gas neon ($Z = 10$), which has its outer shell completed or "satisfied" with 8 electrons. Fluorine has only 7 electrons in its outer shell; sodium, with a total of 11 electrons, has its outer shell of 8 completed and 1 electron to spare. The distribution of electrons in fluorine, therefore, is (2, 7); and in sodium, (2, 8, 1). A sodium and a fluorine atom by combining could make *two* octets, the extra electron from sodium filling the vacant place in the outer shell of fluorine. We should, therefore, predict the compound NaFl which should be a crystalline solid composed of Na^+ and Fl^- ions. In the crystalline form it should be a non-conductor. NaFl is a crys-

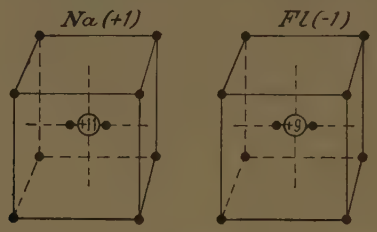


FIG. 105.—A "molecule" of NaFl, illustrating the tendency to form octets.

talline, non-conducting solid with a high melting point (980°C.). We might picture it diagrammatically by Fig. 105, in which the Na^+ ion is made up of a $+11e$ nucleus with its pair of electrons, around which, at the corners of the cube, are the remaining 8 electrons. The fluorine ion is similar, except, perhaps, as to size, but has a ninefold plus charge for its nucleus. The substance NaFl should conduct electrolytically when melted.

Sodium, having 1 electron outside the stable group of 8 which completes the neon structure, should have chemical properties similar to lithium. Both should be monovalent, since they each have a single electron to share. Sodium, like lithium, should be a crystalline, conducting solid. (Its melting point is 97.5°C.)

Fluorine has only 7 electrons in its outside shell. But 2 fluorine atoms, by uniting along an edge so as to hold 2 electrons in common, could form *two* octets, as shown in Fig. 106. This structure should approach in stability the neon structure which it imitates. Thus, fluorine should be a *diatomic* gas with low

boiling point. This is confirmed, the actual boiling point of Fl_2 being $-189°C$.

These combinations of Na and Fl illustrate the tendency to form octets which imitate the stable gas neon.

(*e*) *Carbon* ($Z = 6$); *Nitrogen* ($Z = 7$); *Oxygen* ($Z = 8$).—Oxygen has 6 electrons surrounding its kernel. To make an

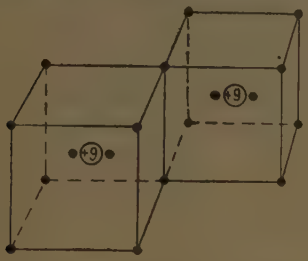


FIG. 106.—The F_2 molecule.

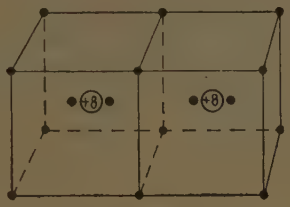


FIG. 107.—The molecule of O_2.

octet 2 more are needed. Oxygen should, therefore, be divalent, and we should expect such compounds as H_2O, Li_2O, Na_2O, etc., since each of the atoms H, Li, and Na have 1 extra electron. Further, 2 atoms of oxygen could combine to form a structure resembling a double octet, as shown in Fig. 107. This combination imitates neon. We should, therefore, expect that oxygen should be a diatomic gas, O_2, and should have a low boiling point.

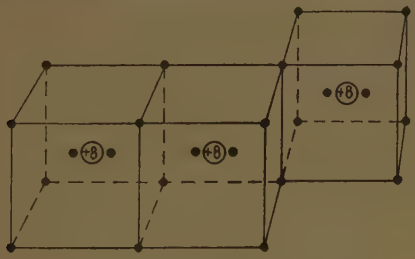


FIG. 108.—The molecule of O_3.

The boiling point of O_2 is actually $-183°C$. By joining another cube to the edge of the double combination shown in Fig. 107, we should predict the gas O_3, as shown in Fig. 108. O_3 has a boiling point of $-112°C$.

The electron from a single hydrogen atom by combining with a single oxygen atom, making the combination OH, would fill seven of the eight places in the outside layer of the oxygen atom,

one place still remaining vacant. The combination OH, therefore, should behave somewhat like fluorine, in that it should be univalent. We would, thus, predict the compound NaOH, which should be made up of Na^+ ions and OH^- ions, as represented in Fig. 109. Actually, NaOH is a solid with a melting point at 318.4°C.

The unique properties of nitrogen are not so easily accounted for. Nitrogen, in molecular form N_2, is a very inactive gas with a very low boiling point (−195°C.). It resembles, somewhat, the inert gases, particularly argon ($Z = 18$). Langmuir assumes that 2 nitrogen atoms combine their 14 electrons as follows: The two kernels account for 4 electrons. Around these two kernels is formed a stable octet, similar to the octet of neon. There are then 2 electrons left over. Langmuir places these with the

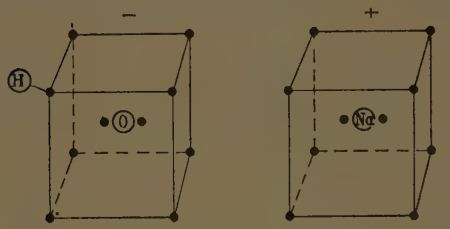


FIG. 109.—The "molecule" of NaOH, showing the ionic, or polar, structure.

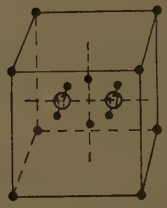


FIG. 110.—Langmuir's suggestion for the structure of N_2.

two kernels in the *inside* of the octet. The whole structure (Fig. 110) externally resembles neon.

The carbon atom with 4 electrons surrounding its kernel is midway between helium and neon. In making pairs or octets, the carbon atom can either share its 4 electrons with other atoms or take on 4 more electrons to complete its octet. We should, therefore, expect the combination CH_4 (methane, boiling point −161°C.), in which the 4 extra electrons necessary to complete the octet surrounding the carbon atom are supplied by the 4 hydrogen atoms, the nuclei of which become attached to four of the corners of the octet. Following Pythagoras(!), we assume that these 4 hydrogen nuclei are *symmetrically* distributed about the octet. The combination CH_2 would be impossible, or at least unstable, since no octet would thereby be formed; but *two* CH_2 groups might unite, somewhat after the manner of 2 oxygen atoms, to form the gas C_2H_4 (ethylene, boiling point −104°C.).

The oxides of carbon and nitrogen are interesting. For example, we have the well-known combinations CO_2 and N_2O. In each of these, after taking out the 6 electrons associated with the three kernels, we have 16 electrons left over to make up the outside structure. Quite irrespective of the particular picture which we draw to represent the 2 molecules, we should expect that the 16 electrons would, in each case, be arranged about the respective three kernels—which are of similar magnitudes as to net positive charge—in such a way as to result in *similar* structures. From this similarity alone, we should expect the 2 molecules CO_2 and N_2O to have similar properties. We may draw

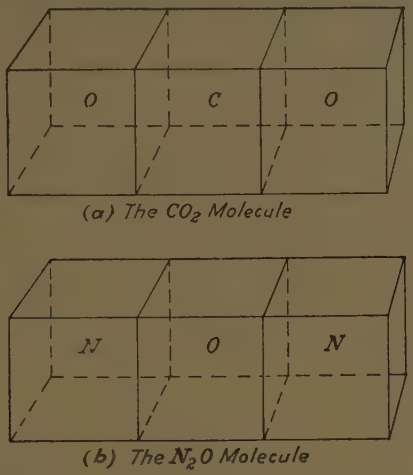


FIG. 111.—Similarity in molecular structure of CO_2 (*a*) and of N_2O (*b*).

pictures (Fig. 111, (*a*) and (*b*)) to help us keep in mind this fact—but the pictures probably bear no relation to the actual appearance of the molecules. From the appearance of the schematic molecules in Fig. 111, we should expect the two substances to be gases not unlike oxygen in thermal properties.

Somewhat similar remarks as to comparative properties may be made regarding the similarity of N_2 and CO, each of which, after accounting for the 4 electrons belonging to the kernels, have 10 electrons grouped around the two kernels. Whether they both have the structure assumed by Langmuir for nitrogen is immaterial—they should have *similar* properties. A comparison of the properties of these pairs of molecules, CO_2 with N_2O and CO with N_2, is shown in Table II.

TABLE II.—COMPARISON OF THE PROPERTIES OF MOLECULES WITH SIMILAR STRUCTURES

	CO_2	N_2O	CO	N_2	O_2	Fl_2
Freezing point, degrees Centigrade	.....	−102.4	−207	−209.8	−218.4	−223
Boiling point, degrees Centigrade	−78.5	− 89.5	−192	−195.8	−183.0	−187
Critical pressure, atmospheres	77	75	35	33	50	
Critical temperature, degrees Centigrade	32	35	−151	−146	−118	
Critical volume, cm.^{3} per gram	2.2	2.4	5.05	5.17	1.5	
Viscosity at 20° Centigrade	$148 \cdot 10^{-6}$	$148 \cdot 10^{-6}$	$163 \cdot 10^{-6}$	$166 \cdot 10^{-6}$	$187 \cdot 10^{-6}$	
Density of liquid at boiling point	.....	.....	0.793	0.796	1.14	1.11
Index of refraction (liquid)	1.190	1.193	.....	1.197	1.221	

It may be pointed out that, while the theory predicts that these substances ought to have *similar* properties, there is no suggestion whatever of a method of *computing* those properties from fundamental constants or even of making a *quantitative* comparison with the properties of the inert gases. Further, the similarity loses some of its significance when it is observed that the properties of O_2 and of Fl_2 are quite similar, although these two molecules are assumed to have dissimilar structure (see Figs. 106 and 107).

Nitrogen, with a total of 7 electrons, 3 short of enough to complete an octet surrounding the kernel, could combine with 3 hydrogen atoms, making the molecule NH_3 (ammonia) which should have a neon-like structure, except for the 3 hydrogen nuclei attached to three corners. Ammonia should have a low boiling point. Actually, its boiling point is − 33, and its freezing point is −78°C.

One would not expect that 4 hydrogen atoms could combine with a nitrogen atom to make a *stable* combination, since there is 1 more electron than enough to make an octet. We might expect, however, that 4 hydrogen atoms together with a nitrogen atom might behave much like sodium toward combining with either an atom or a combination of atoms which lacks 1 electron to complete an octet. Thus, we should predict the well-known ammonium (NH_4) compounds, the ammonium forming the positive ion, as in $(NH_4)^+ + (OH)^-$.

The student will find it interesting and, up to a certain point, instructive to "build" other molecular models by use of this general principle that combinations tend to take place in such a way as to form pairs or octets. The illustrations which have been given are sufficient to indicate the importance of this principle in any theory which has to do with the distribution of electrons in atoms.

(*f*) *Magnesium* ($Z = 12$); *Silicon* ($Z = 14$); *Phosphorus* ($Z = 15$).—The properties of magnesium are determined largely by the fact that it has 2 electrons more than enough to complete the octet. We may assume that its structure is represented by (2, 8, 2). Hence, we should expect such stable combinations as MgO—periclase (melting point 2800°C.)—and MgF_2 (melting point 1400°C.).

Silicon, with 4 electrons in addition to the underlying octet and with a probable structure (2, 8, 4), should behave much like carbon. Thus, we have SiO_2 (quartz), SiH_4 (gas, melting point -185; boiling point -112°C.), and SiF_4 (silicon tetrafluoride, melting point -77; boiling point -65°C. under $2\frac{1}{2}$ atmospheres).

Phosphorus (assumed structure (2, 8, 5)) like nitrogen lacks 3 electrons of filling an octet (the *second* octet for phosphorus). The properties of phosphorus should, therefore, be somewhat similar to those of nitrogen in the formation of compounds. Thus, we have the well-known gas PH_3—phosphine—analogous to NH_3. Because of the greater charge on the nucleus, however, and the greater number of electrons involved, one would not expect 2 phosphorus atoms to unite to form a neon-like structure as was postulated for N_2 (Fig. 110). Langmuir[1] discusses many of the compounds in which phosphorus enters.

3. The Heavier Elements. (*a*) *General Factors Determining Chemical and Spectroscopic Properties.*—Passing by, for the moment, the question of how the electrons are distributed in the atoms of the heavier inert gases—Ar(18), Kr(36), Xe(54), and Nt(86)—but taking it as an *experimental fact* that their structures are stable, one readily sees that the next element beyond any one of the permanent gases should have 1 more than enough electrons to form a stable structure. These elements, together with lithium and sodium, are the metals of the alkali group—K(39), Rb(37), Cs(55)—the chemical properties of which are strikingly similar. The *second* element beyond a permanent

[1] *Jour. Amer. Chem. Soc.*, vol. 38, p. 762 (1916).

gas should have 2 superfluous electrons. Hence, we have the series of similar elements, commonly divalent—Mg(12), Ca(20), Sr(38), Ba(56), Ra(88). Going in the other direction, the next element *before* a perfect gas lacks 1 electron of enough to make a stable structure. These elements are the halogens—F(9), Cl(17), Br(35), I(53), and perhaps the undiscovered element (85). The series of elements next preceding the halogens are O(8), S(16), Se(34), Te(52). These, likewise, are similar.

The prediction of the *similarities* of these series of elements is quite independent of any assumption concerning the structure of the atom of the neighboring inert gas. Calcium and barium, for example, are similar, whatever their *internal* electron structures may be, simply because they have 2 electrons outside the stable shells corresponding to the "surface" layer of the preceding inert gases. These gases themselves are inert, so we believe, because, in addition to their stable internal structures, they possess completed, or satisfied, superficial groups of electrons. A comparison of the series systems of spectra in these groups of chemically similar elements shows that they have similar spectra. The spectral series (arc spectra) of the alkali elements consist of doublets; in the arc spectra of the elements of the Mg-Ca-Sr-Ba group are found two systems of lines: a complete *singlet* system containing *S*, *P*, *D*, and *F* terms and a similarly complete *triplet* system. Other groups of elements in the periodic table show like regularities as regards the multiplicity of their spectra. Also, the *spark* spectra of the *alkali* metals (*i.e.*, the *additional* lines brought out by the more intense *spark* discharge) are very similar to the *arc* spectra, respectively, *of the previous inert gases;* and the *spark* spectra of the elements of the Mg-Ba group are similar, in turn, to the *arc* spectra of the previous alkali metal. We may ascribe spark spectra as originating in atoms which, on account of the intensity of the excitation to which they have been subjected, have lost 2 electrons, instead of only 1 as in arc spectra. This similarity between the *spark* spectrum of an element and the *arc* spectrum of the element of next lowest atomic number is, thus, quite understandable, since, for example, a Sr(38) atom which has lost 2 electrons should be very similar to a Rb(37) atom which has lost only 1 electron, the two structures Sr_{II} and Rb_{I} having the same *total* number of extranuclear electrons and differing mainly in the magnitude of the nuclear charges.

All these similarities, both chemical and spectroscopic, suggest a very fundamental principle, which we shall find useful in discussing further the arrangement of electrons in atoms, namely, that *the chemical and the spectroscopic*[1] *properties of an atom are determined much more by the number and the arrangement of the electrons in the outside shell than by the total number of electrons in the atom.* Conversely, by studying the chemical and spectroscopic properties of atoms, we may obtain information as to the number of electrons in the surface layer, but not the number or arrangement in inside layers. This latter information regarding the more deeply lying electrons comes largely from X-ray phenomena, which we shall discuss in the next chapter.

In support of this general principle, one may compare one by one the elements Li to Ne inclusive with the corresponding elements in the sequence, Na to A inclusive. Li and Na are similar because they each have 1 more electron than enough to complete a stable structure; Be and Mg each have 2 "superfluous" electrons; B and Al have 3; C and Si have 4; etc.

For making this comparison clear, the periodic arrangement of the elements as proposed by Bohr (Appendix 1(*c*)) is useful. In this diagram, the elements are arranged in periods, a period constituting the sequence of elements from one inert gas to and including the next. The first period contains H and He. Period II, the first "short period," extends from Li to Ne; and Period III, the second short period, from Na to Ar. Then come two *long* periods of 18 elements each, K(19) to Kr(36) and Rb(37) to Xe(54). Period VI, sometimes called the "rare-earth period," contains 36 elements, Cs(55) to Nt(86). The last period, VII, is incomplete (at least among terrestrial elements).

(*b*) *The Elements of the Fourth Period.*—The elements of Period II—Li(3), Be(4) . . . Ne(10)—contain, respectively, in the outside shell 1, 2 . . . 8 electrons. Similarly, the outside shells of the corresponding elements of Period III contain 1, 2 . . . 8 electrons. Comparing those elements which have identical numbers of electrons in the outside shell, we find that Li is similar to Na; Be is similar to Mg . . . N is similar to P; and so on. These similarities are indicated by the horizontal lines between the respective members of the two periods in Appendix I(*c*).

[1] "Spectroscopic," as here used, is limited to that part of the spectrum in the neighborhood of the visible region.

Comparing Period III with Period IV, we find that Na is similar to K; Mg is similar to Ca. Beginning with Sc(21), in Period IV, however, the similarity with the corresponding element in group III becomes less. Scandium (21), with 3 electrons more than enough to complete the second stable group of 8, is somewhat similar to Al(13) and Boron (5). All are, commonly, trivalent. Thus, we have the oxides B_2O_3, Al_2O_3, Sc_2O_3 and the chlorides BCl_3, $AlCl_3$, $ScCl_3$. But a further comparison of properties shows that the similarity in chemical behavior is not so great as might be expected if the extra 3 electrons were *identically* arranged in the three elements. They differ in their hydrates and in the solubilities of some of their salts. Differences of this sort increase as one goes farther down the two periods. In general, the elements of Period IV, between Sc(21) and Co(27), show a greater tendency to variable valency than corresponding elements in Period IV. Furthermore, the magnetic elements iron, cobalt, and nickel have no analogues in Period III. In addition to their being magnetic, these three magnetic elements are similar to each other in other respects. They have, in addition to variable valency, many similar hydrates of their various salts; thus:

$FeSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$
$NiSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$
$CoSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4 \cdot CoSO_4 \cdot 6H_2O$

Beginning at the other end of the two periods and working backward, the similarity extends for several elements. Preceding the inert gases argon(18) and krypton(36) come the halogens chlorine(17) and bromine(35). Preceding these in turn are the similar elements sulphur (16) and selenium (34). Then come phosphorus (15) and arsenic(33); silicon(14) and germanium (32); aluminum(13) and gallium (31). Magnesium (12), although very similar to calcium (20), the *second* member of group IV, is also very similar to zinc(30). Magnesium and zinc are both divalent and form very similar compounds. The arc spectrum of zinc contains a complete system of triplets and another complete system of singlets, just as do the corresponding spectra of the members of the Mg-Ba group of elements. Both chemical and spectroscopic evidence indicates that the *external* electron structure of the zinc atom should be similar to the structures of magnesium and calcium. These latter elements, being, in each

case, the second beyond an inert gas, *probably* have 2 electrons outside of the outermost stable group of 8. The conclusion is obvious, therefore, that zinc, although in the *middle* of the period, contains 2 electrons outside of a *stable* group. Now, zinc has 30 extranuclear electrons. If we represent the structure of Mg(12) by (2, 8, 2) and of Ca(20) by (2, 8, 8, 2), Zn(30) should, similarly, be (2, 8, 18, 2), *the third shell containing* 18 *electrons.*

Copper, immediately preceding zinc, has a spectral-series system containing doublets, just as have the alkali elements. This, together with the fact that in the well-known series of cuprous compounds copper is monovalent, suggests the structure for copper (2, 8, 18, 1), with the alternative for divalent copper (2, 8, 17, 2). Comparing either of these with the structure of calcium (2, 8, 8, 2), we see that in Period IV, after passing calcium, electrons in the succeeding elements, instead of being added to the *fourth* shell, have been added to the *third* shell, increasing the latter from 8, in the case of calcium, to 18, in the case of copper and magnesium. After the third shell has been built up to 18 electrons, there seems to be no further tendency for it to increase, since the elements of Period IV, following zinc, have analogues in Period III in the elements following magnesium. Taking the structure of silicon (14) to be (2, 8, 4), that of the analogous element in Period IV, namely, germanium (32), should be (2, 8, 18, 4). Similarly, we should expect for selenium (34) the structure (2, 8, 18, 6); and, finally, for krypton (2, 8, 18, 8). Thus, in krypton, as in argon, the *outer* shell contains 8 electrons. The sequence of numbers as suggested by Rydberg (p. 415) still holds, only *we must invert the order of the last two, viz.*, $2(1^2 + 2^2 + 3^2 + 2^2)$.

It appears, therefore, that the elements scandium to nickel inclusive, in Period IV, form a *transition* series during which the number of electrons in the third shell is being built up from 8 to 18. (These are the elements of Period IV enclosed in the rectangle in Appendix I(*c*).) Bury[1] makes the following postulate:

> The maximum number of electrons in the outer layer of an atom is 8; more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18 (as from scandium to nickel) or from 18 to 32, there occurs a transition series of elements which can have more than one structure.

[1] *Jour. Amer. Chem. Soc.*, vol. 43, p. 1602 (1921).

That is to say, the elements in this transition series have variable valencies, as is illustrated by the various oxides of manganese. Bury proposes the following as possible structures for some of the elements of this transition series:

Cr(24): (2, 8, 8, 6); (2, 8, 11, 3); (2, 8, 12, 2)
Mn(25): (2, 8, 8, 7); (2, 8, 11, 4); (2, 8, 12, 3); (2, 8, 13, 2)
Fe(26): (2, 8, 10, 6); . . . ; (2, 8, 12, 4); (2, 8, 13, 3)

(*c*) *Period V, the Second "Long Period."*—This period contains exactly the same number of elements, namely 18, as the preceding period, Period IV. Arguing from the similarities of the respective elements in Periods II and III, each of which contains *eight* elements, we may infer that each element of group V should have a homologous element in Period IV. This proves to be the case. At the beginning of the periods, we have the alkali elements K and Rb. Next come the alkaline earths Ca and Sr. Chromium (24) and molybdenum (42) both form very similar compounds. Corresponding to the elements Fe, Co, Ni, in Period IV, are the elements Ru, Rh, Pd, in Period V. Although the latter are not ferromagnetic, they have many chemical similarities to the magnetic elements Fe, Co, Ni. Ag (47) is similar to Cu (29) as regards both chemical and spectroscopic properties. The similarity continues, growing more striking, until we reach the end of the period.

This similarity of the elements of Period V with corresponding elements of Period IV leads to the belief that we have, in Period V, transitions in electron arrangements similar to those found in Period IV. Accordingly, Rb(37) should have the structure (2, 8, 18, 8, 1); Sr (38), the structure (2, 8, 18, 8, 2). Then comes the "transition series," Y(39) to Pd(46), in which the fourth shell is being built up from 8 to 18 electrons. Ag(47) should have a structure (2, 8, 18, 18, 1); Cd(48), (2, 8, 18, 18, 2); . . . I(53), (2, 8, 18, 18, 7); and Xe(54), (2, 8, 18, 18, 8). Again we find that the stable *outside* layer contains 8 electrons. We may write the Rydberg series of numbers for xenon: $2(1^2 + 2^2 + 3^2 + 3^2 + 2^2)$.

(*d*) *Period VI, the Rare-earth Period.*—The first two elements of this period, namely, cesium (55) and barium (56), are exactly analogous to the first two elements of each of the preceding periods, and we may predict the respective structures (2, 8, 18,

18, 8, 1) and (2, 8, 18, 18, 8, 2). Beginning with lanthanum (57) and extending through (and including) platinum(78), two important transition series are found: (1) the first transition series[1] in which the *fourth* shell, containing 18 electrons in lanthanum, is built up to 32 electrons from lanthanum to-lutecium (71); (2) the second transition series, hafnium (72) to platinum (78), in which the *fifth* layer, containing probably 9 electrons in lutecium, is built up to 18 in platinum, which number, by comparison with xenon at the end of Period V, should give a stable combination. With gold (79) begins the building up of the sixth, or outside, layer of the elements of Period VI, to 8 electrons, a process which is complete with nitron (86). The structure of Nt should, thus, be (2, 8, 18, 32, 18, 8). This distribution of electrons among the several layers is again represented by Rydberg's series of squared integers, by rearrangement, *viz.*, $2(1^2 + 2^2 + 3^2 + 4^2 + 3^2 + 2^2)$.

(*e*) *The Seventh Period.*—This period contains only three well-known elements—radium (88), thorium (90), and uranium (92). The unknown element (87), should be similar to the alkali elements. Radium is similar to the elements of the Mg-Ba group. With actinum (89) probably begins the building up of the *sixth* shell from 8 electrons in radium to 12 electrons in uranium, the last of the known elements. The structure of radium should be (2, 8, 18, 32, 18, 8, 2); of uranium, (2, 8, 18, 32, 18, 12, 2).

(*f*) Table III, reproduced, in part, from similar tables based on spectroscopic data, shows the distribution of electrons in the various levels for all the atoms of the periodic table. The arrangement is similar to Bohr's table (Appendix I(*c*)), in that all the elements of a given period are arranged in one column. The several groups of electrons in each element are designated by a number $n = 1, 2, 3 \ldots$, as shown at the top of each column. This number n may be identified with the total quantum number τ of the successive orbits in Bohr's scheme as discussed in Sec. 5, below.

We shall see in Sec. 5 that it is necessary still further to subdivide the groups of electrons which we have here designated by n.

[1] The elements of this transition series, the rare earths, are similar to the transition series Se to Ni of Period IV but, according to Bury, "do not show the variety of structure" characteristic of the latter series.

TABLE III.—THE DISTRIBUTION OF ELECTRONS IN ORBITS CHARACTERIZED BY TOTAL QUANTUM NUMBER n

Period I		Period II			Period III			
n =	1	n =	1	2	■ =	1	2	3
H	1	Li	2	1	Na	2	8	1
He	2	Be	2	2	Mg	2	8	2
		Bo	2	3	Al	2	8	3
		C	2	4	Si	2	8	4
		N	2	5	P	2	8	5
		O	2	6	S	2	8	6
		F	2	7	Cl	2	8	7
		Ne	2	8	Ar	2	8	8

Period IV					Period V					
n =	1	2	3	4	n =	1	2	■	4	5
K	2	8	8	1	Rb	2	8	18	8	1
Ca	2	8	8	2	Sr	2	8	18	8	2
Sc	2	8	9	2	Y	2	8	18	9	2
Ti	2	8	10	2	Zr	2	8	18	10	2
V	2	8	11	2	Nb	2	8	18	12	1
Cr	2	8	13	1	Mo	2	8	18	13	1
Mn	2	8	13	2	Ma	2	8	18	14	1
Fe	2	8	14	2	Ru	2	8	18	15	1
Co	2	8	15	2	Rh	2	8	18	16	1
Ni	2	8	16	2	Pd	2	8	18	18	
Cu	2	8	18	1	Ag	2	8	18	18	1
Zn	2	8	18	2	Cd	2	8	18	18	2
Ga	2	8	18	3	In	2	8	18	18	3
Ge	2	8	18	4	Sn	2	8	18	18	4
As	2	8	18	5	Sb	2	8	18	18	5
Se	2	8	18	6	Te	2	8	18	18	6
Br	2	8	18	7	I	2	8	18	18	7
Kr	2	8	18	8	Xe	2	8	18	18	8

Period VI							Period VII							
■ =	1	2	3	4	5	6	n =	1	2	3	4	5	6	7
Cs	2	8	18	18	8	1	...	2	8	18	32	18	8	1
Ba	2	8	18	18	8	2	Ra	2	8	18	32	18	8	2
La	2	8	18	18	9	2	Ac	2	8	18	32	18	9	2
Ce	2	8	18	19	9	2	Th	2	8	18	32	18	10	2
Pr	2	8	18	20	9	2	Pa	2	8	18	32	18	11	2
Nd	2	8	18	21	9	2	U	2	8	18	32	18	12	2
Il	2	8	18	22	9	2								
Sa	2	8	18	23	9	2								
Eu	2	8	18	24	9	2								
Gd	2	8	18	25	9	2								
Tb	2	8	18	26	9	2								
Dy	2	8	18	27	9	2								
Ho	2	8	18	28	9	2								
Er	2	8	18	29	9	2								
Tu	2	8	18	30	9	2								
Yb	2	8	18	31	9	2								
Lu	2	8	18	32	9	2								
Hf	2	8	18	32	10	2								
Ta	2	8	18	32	11	2								
W	2	8	18	32	12	2								
Re	2	8	18	32	13	2								
Os	2	8	18	32	14	2								
Ir	2	8	18	32	15	2								
Pt	2	8	18	32	16	2								
Au	2	8	18	32	18	1								
Hg	2	8	18	32	18	2								
Tl	2	8	18	32	18	3								
Pb	2	8	18	32	18	4								
Bi	2	8	18	32	18	5								
Po	2	8	18	32	18	6								
...	2	8	18	32	18	7								
Nt	2	8	18	32	18	8								

PART II. THE DYNAMIC ATOM MODEL

4. The Problem of the Distribution of Electrons in Orbits.— By considerations based largely on optical spectra, Bohr[1] proposed, regarding the distribution of electrons in the various possible *orbits* surrounding a nucleus, a system which, in its general features, is somewhat similar to that proposed by Bury for the distribution of electrons in various levels or shells. Bohr assumes that around a nucleus of atomic number Z there are, in the normal, neutral atom Z electrons revolving in orbits which are characterized by radial and azimuthal quantum numbers. Using the terminology suggested on page 372, there are around each nucleus various "privileged" orbits designated, respectively, by 1_1, 2_1, 2_2, 3_1, 3_2, 3_3, 4_1 . . . (The number stands for the *total* quantum number $n \equiv \tau$, and the subscript for the azimuthal quantum number $k \equiv \tau_\phi$. Thus, a 3_2 orbit is an orbit of total quantum number 3, azimuthal quantum number 2, and radial quantum number 1. In general, an orbit is designated by n_k, where n is the total quantum number and k the azimuthal quantum number.)

We saw, in Chap. X, equation (80′), that the energy $W_{n,k}$ of an n_k orbit around a nucleus of charge Z is given by the equation

$$W_{n,k} = -\frac{2\pi^2 m Z^2 e^4}{h^2}\left[\frac{1}{n^2} + \frac{1}{n^4}\cdot\frac{4\pi^2 Z^2 e^4}{c^2 h^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right] \qquad (2)$$

This equation is equivalent to equation (80′), Chap. X. The changes in symbols are as follows:

$$(\tau_r + \tau_\phi) \equiv n;\ \tau_\phi \equiv k.$$

For a given nuclear charge Z, the larger the total quantum number n the greater (*algebraically*) is the energy of the orbit; and for a given value of n, the energy is greater the greater k; *i.e.*, orbits of a given quantum number n are at a higher energy level the less the eccentricity. This, however, applies only to the case of a nucleus and a *single* electron in an n_k orbit. The situation is much more complex if the nucleus is surrounded by other electrons; as previously pointed out, it is then impossible to obtain a rigorous expression for W.

The method, initiated by Bohr and developed by him and others, of assigning electrons to various orbits on the basis of

[1] BOHR, N.: "The Theory of Spectra and Atomic Constitution," Chap. III.

spectroscopic data consists in picturing the sequence of events in a hypothetical experiment in which a nucleus of charge $+Ze$, initially stripped of all its electrons, acquires one by one the Z electrons necessary to make a neutral atom. Bohr assumes that in this process each added electron goes into such a *vacant permissible* orbit as makes the energy of the system, after that electron has been added, a minimum, a condition which is assumed to give greatest stability. In deciding which orbit the next "captured" electron will permanently occupy, Bohr is guided, in part, by equation (2) and, in part, by the terms in the optical spectra, arc and spark, of the element concerned. We shall discuss very sketchily in the next section some of the factors which are considered in ascertaining which orbits the various electrons in the normal atoms occupy.

5. Some Examples Illustrative of the Spectroscopic Method. (*a*) *Hydrogen.*—The orbit of lowest level is, of course, the 1_1 orbit, *i.e.*, the circle of total quantum number 1. Hence, the electron captured by a hydrogen nucleus ultimately reaches and, in the normal atom, continues to move in the 1_1 orbit.

(*b*) *Lithium; Effective Quantum Numbers.*—Passing by the arguments by which Bohr concludes that both of the electrons in helium move in 1_1 orbits, we come to lithium. The first two electrons captured by the lithium nucleus will, according to Bohr, occupy the two possible 1_1 orbits as in the case of helium. We know from chemical data that the third electron of lithium is much less closely bound than are the first two —a fact which, in the orbit scheme, suggests that the third electron revolves in an orbit of total quantum number larger than 1, probably in a 2_1 orbit, since this would give to the lithium atom a *lower* energy than if the third electron were to occupy a 2_2 orbit. This surmise is strengthened by considering the spectrum of lithium.

FIG. 112.—The kernel of the lithium atom with its net charge of $+e$ should behave as a single-charged nucleus toward the third more distant electron *c*.

Lithium, in common with the other alkali elements, has four sequences of terms—*S*, *P*, *D*, and *F* terms—the combinations of which give rise to the four main series—*principal*, *sharp*, *diffuse*, and *fundamental*. Although we cannot apply to the lithium atom any equation of the type of equation (2) for the determination of the terms from fundamental constants, we can make some qualitative inferences based on the equation. The lithium nucleus,

with its two close-in electrons a and b, (Fig. 112) revolving in 1_1 orbits, will behave toward a third electron c at a *greater* distance from the nucleus *almost* as if the nucleus together with a and b constituted a *single* positive charge $+e$. Or, we may say that a and b partially *screen* the nucleus, so that its *effective* charge is less than $+3$, so far, at least, as concerns points at considerably greater distances from the nucleus than the radius of the 1_1 orbits. Accordingly, if the lithium atom be ionized by the removal of electron c, we should expect that the resulting spectrum when the electron is recaptured would be "hydrogen-like," at least for interorbital transfers involving quantum numbers of, say, 3 or larger.

Now, we obtain the *terms* of the *hydrogen* spectrum by dividing the Rydberg constant N_∞ by the square of the total quantum numbers n of the orbits—speaking, for the moment, only of circular orbits—thus the expression:

$$\frac{N_\infty}{n^2}$$

where n stands for the successive integers 1, 2, 3 . . . , gives the *terms* of the hydrogen spectrum. In spectra other than hydrogen, the terms are obtained by dividing N_∞ by such quantities as $(m + \mu)^2$, where m is an integer and μ is a constant. Thus, the π terms in the spectra of the alkali elements are given by (see Chap. IX)

$$\pi(m) = \frac{N_\infty}{(m + \pi)^2}.$$

By comparison with the hydrogen spectrum, we may think of the quantity $(m + \pi)$ as the *effective* quantum number n_e of the term. Knowing the values of the terms, say in wave numbers, from spectral-series data, the *effective* quantum number can be obtained at once by the relation

$$\text{Term value} = \frac{N_\infty}{n_e^2}$$

The wave numbers of the S, P, D, and F terms in the spectrum of lithium[1] are given in Table IV, together with the computed *effective* quantum numbers.

[1] Data taken from Fowler's report.

TABLE IV.—EFFECTIVE QUANTUM NUMBERS n_e IN LITHIUM. $N_\infty = 109{,}720$

S terms		*P* terms		*D* terms		*F* terms	
Wave number	n_e	Wave number	n_e	Wave number	n_e	Wave number	n_e
43,486	1.588	28,582	1.959	12,203	2.998	6,856	4.000
16,280	2.595	12,560	2.955	6.863	3.998	4,382	5.003
8,475	3.598	7,018	3.953	4,390	4.999		
5,187	4.599	4,474	4.952	3,047	6.000		

The effective quantum numbers, *computed directly from spectral data*, for the two *F* terms *are seen to be almost exactly* the integers 4 and 5. These two terms correspond very closely to terms which would be computed for a *hydrogen* nucleus for the quantum numbers 4 and 5. The inferences, therefore, seem justified (1) that these two *F* terms correspond to *actual* quantum numbers 4 and 5, the *lowest F* term having quantum number 4; and (2) that for the corresponding orbits we may regard the core (+3 nucleus and 2 electrons) of the lithium atom as *equivalent* to a single-charged, hydrogen-like nucleus. For these orbits, the inverse-square law, therefore, holds, since the inverse-square law was assumed for the hydrogen orbits.

Likewise, the effective quantum numbers of the *D* terms are *very nearly* the respective integers 3, 4, 5, 6; from which we may infer that the *lowest D* term has quantum number 3 and corresponds to a circular orbit $n = 3$.

The effective quantum numbers for the *P* terms are a little *less* than the respective integers 2, 3, 4, 5. This corresponds to a stronger "binding" of the electron in the respective orbits than if the numbers were *exactly* 2, 3, 4, 5. We may think of this increased binding in these orbits, particularly orbit number 2, as resulting from an *increase* in the *effective* nuclear charge, which, in turn, is due to a *decrease* in the *screening effect* of the 2 electrons in 1_1 orbits.

The *S* terms have effective quantum numbers which differ considerably from integers. To what orbit may we assign the lowest *S* term, for which the effective quantum number is 1.588? Not to a 2-quantum orbit, of the same kind as the lowest *P* term, since the binding is considerably stronger than that of the lowest *P* term; not to a 1_1 orbit, since the binding is not so strong as it

is for the first 2 electrons. The next orbit above the 1_1 orbit is the 2_1 orbit, the ellipse. We may *guess* that the lowest S term, therefore, corresponds to a 2_1 orbit and that the lowest P term corresponds to a 2_2 orbit.

The difference in energy between the lowest S term and the lowest P term, however, $-43{,}486$ as against $28{,}582$—is greater than equation (2) (see, also, equation (83)) leads us to expect for the difference in energy between the 2_1 and the 2_2 orbit. If these two terms correspond to the suggested orbits, how can the great difference in energy be explained? The explanation involves a very fundamental principle. The 2_2 orbit is a circle of quantum number 2. It is symmetrically situated with respect to the core of the atom and is in a field which departs only a little from the inverse-square law, since its effective quantum number is very nearly 2. On the contrary, the 2_1 orbit is an ellipse. At perihelion, the electron is much closer to the nucleus than is any part of the 2_2 orbit. We see that even with the 2_2 orbit the screening effect of the two core electrons becomes less than with orbits of higher quantum number, and, accordingly, we should expect the perihelion part of the 2_1 orbit to be much less screened by the first 2 electrons than is any part of the 2_2 orbit. An electron in the 2_1 orbit should, therefore, be much more strongly bound than one in the 2_2 orbit.

This penetration of elliptical orbits of higher quantum number into the orbits of lower quantum number and of lower eccentricity results in a much greater binding energy for the more eccentric orbits than for the lesser eccentric orbits of the same total quantum number. It may even happen in elements of higher atomic number that the binding energy corresponding to an eccentric orbit of given quantum number, such as a 5_1 orbit, may become greater than the binding energy corresponding to a lesser eccentric orbit, say a 4_3 orbit, of *lower* quantum number.

Now, since the first S term is the *lowest* observed term in the arc spectrum of lithium, we may assume that the orbit corresponding to this term—the 2_1 orbit—is *the lowest orbit reached by the third electron of lithium.* Or, we might say that the 2_1 orbit is the *basic* orbit for the third electron. We conclude, therefore, that the *first* 2 electrons in lithium normally occupy 1_1 orbits; and the third, a 2_1 orbit.

Returning to the lowest D and F terms, we conclude that since their effective quantum numbers are integers, the orbits

lie entirely in an inverse-square field and either are circular or are ellipses of low eccentricity. For otherwise we should expect a marked departure of the effective quantum numbers from integer values, as occurs in the case of the 2_1 orbit. We may guess, provisionally, that the lowest D orbit, therefore, is a 3_3 orbit; and the lowest F orbit, a 4_4 orbit.

The orbits corresponding to the *lowest* terms in each of the four sequences S, P, D, and F are, thus, respectively, 2_1, 2_2, 3_3, 4_4. The azimuthal quantum numbers (*i.e.*, subscripts) of these orbits are seen to be, respectively, 1, 2, 3, 4. There is evidence to support the view that the higher terms of a sequence have the same azimuthal quantum number as the lowest term of the sequence but that the *total* quantum number presumably increases by unity from one term to the next. Thus, the orbits corresponding to the S sequence in lithium should be 2_1, 3_1, 4_1, . . . There is considerable uncertainty in the assignment of the total quantum number to the spectral terms in the several elements. There is less ambiguity regarding the azimuthal quantum numbers.

(*c*) *Sodium, Potassium, Rubidium, and Cesium.*—We pass on to the other alkali elements. From the similarity of their spectra with that of lithium, which we ascribed to the binding of the third electron, we may conclude that the spectra of sodium, potassium, rubidium, and cesium arise, also, from the process of binding a *single* electron, namely, the eleventh, nineteenth, thirty-seventh, and fifty-fifth, respectively. We saw from the discussion of the lithium spectrum that much information may be gained concerning orbits from a consideration of the *effective* quantum numbers of the terms of the several sequences. When an atom has lost 1 electron, the remainder of the atom—the core—has a net positive charge $+e$, exactly the same as has the hydrogen nucleus. The hydrogen nucleus is surrounded by an inverse-square field—sometimes called a "coulombian field," from Coulomb's law—and the terms in the hydrogen spectrum have integer quantum numbers. When we find that the terms of a sequence in the spectrum of some other element have *effective* quantum numbers which are successive *integers* (as the F terms in lithium), we conclude that the corresponding orbits (1) lie in an inverse-square, or *coulombian*, field and (2) do not penetrate the more deeply lying orbits. Conversely, a material departure of the effective quantum number from an expected integer value indicates a stronger binding of an electron in that

orbit due either to interpenetration of the orbit or to some other departure from the inverse-square law.

Table V gives the effective quantum numbers of the first four terms in the S, P, D, and F sequences in the alkali elements, computed from term values in the same way as for lithium in Table IV.

TABLE V.—EFFECTIVE QUANTUM NUMBERS AND CORRESPONDING ORBITS FOR THE TERMS IN THE SPECTRA OF THE ALKALI ELEMENTS

Term number	Effective quantum numbers				Corresponding orbits			
	S	*P*	*D*	*F*	*S*	*P*	*D*	*F*
				Na				
1	1.63	2.12	2.99	4.00	3_1	3_2	3_3	4_4
2	2.64	3.13	3.99	5.00	4_1	4_2	4_3	5_4
3	3.65	4.14	4.99	6.00	5_1	5_2	5_3	6_4
4	4.66	5.14	5.99	....	6_1	6_2	6_3	7_4
				K				
1	1.77	2.24	2.85	3.99	4_1	4_2	3_3	4_4
2	2.80	3.26	3.79	4.99	5_1	5_2	4_3	5_4
3	3.81	4.27	4.76	5.99	6_1	6_2	5_3	6_4
4	4.81	5.27	5.75	6.99	7_1	7_2	6_3	7_4
				Rb				
1	1.80	2.29	2.76	3.99	5_1	5_2	3_3	4_4
2	2.84	3.32	3.70	4.98	6_1	6_2	4_3	5_4
3	3.85	4.34	4.68	5.97	7_1	7_2	5_3	6_4
4	4.85	5.35	5.67	6.97	8_1	8_2	6_3	7_4
				Cs				
1	1.87	2.36	2.55	3.97	6_1	6_2	3_3	4_4
2	2.91	3.40	3.52	4.97	7_1	7_2	4_3	5_4
3	3.93	4.42	4.52	5.97	8_1	8_2	5_3	6_4
4	4.94	5.42	5.52	6.97	9_1	9_2	6_3	7_4

In sodium, the F terms have the integer values 4, 5, 6 . . . As in lithium, we may assume that these orbits are 4_4, 5_4, 6_4 . . . and that they do not penetrate the sodium *core*, which presumably differs from the structure of the previous inert gas (neon) only in having a nuclear charge of $+11e$. The D terms

differ only slightly from the integers expected for "hydrogen-like" terms, and we conclude that the *D* orbits are similar to those in lithium, namely 3_3, 4_3, 5_3 . . .

The effective quantum number of the lowest *P* term *exceeds* 2. Since departure from the inverse-square law should make the effective quantum number *less*, instead of *greater*, than that of the corresponding hydrogen term, we assume that the quantum number of the first *P* term is 3 in sodium. (It was 2 in lithium.) Since the binding of this first *P* orbit is greater than that of the first *D* orbit, which is a 3_3 orbit, the first *P* orbit must be a 3_2 orbit, and the succeeding *P* terms correspond to 4_2, 5_2, 6_2 . . . orbits.

The effective quantum number of first *S* term, *the lowest in the arc spectrum of sodium*, departs *less* from the integer 2 than did the first term of the *S* sequence in lithium, although, because of the much larger core of sodium and the greater nuclear charge, there should be *more* deviation from the corresponding hydrogen quantum number than in lithium. If, however, we assume that the first *S* term of sodium corresponds to an orbit of quantum number 3, instead of to an orbit of the quantum number 2, as in lithium, we provide for the expected greater departure. If this be correct, the first *S* orbit in sodium—the basic orbit, since it is the lowest—must be a 3_1 orbit. This is the orbit, then, into which the eleventh electron of sodium finally "settles."

It is pertinent to inquire at this point, In what orbits are the other 10 electrons of sodium to be found? The first 2 occupy 1_1 orbits, and the third a 2_1 orbit, as in lithium. The remaining 7 *presumably* are distributed among 2_1 and 2_2 orbits, since they must all be more closely bound than is the eleventh electron, which occupies a 3_1 orbit. We shall say a word, presently, about the distribution of these 7 electrons in the 2_1 and 2_2 orbits.

From a similar study of the effective quantum numbers in the other alkali elements, we may conclude that the *basic* orbits of the nineteenth electron in potassium, the thirty-seventh in rubidium, and the fifty-fifth in cesium are, respectively, 4_1, 5_1, and 6_1.

(*d*) *Magnesium and Aluminum.*—Magnesium has 12 electrons — 1 more than sodium. The spectrum of Mg_I[1] consists of a

[1] That is, the arc spectrum of magnesium. This is the spectrum produced when Mg_I, which is the magnesium "core" remaining after neutral magnesium has lost 1 electron, recaptures the twelfth electron.

complete system of triplets and a complete system of singlets. The three lowest terms are (in wave numbers)

$$1S \text{ (singlet)}: 61{,}672.1$$
$$1p_3 \text{ (triplet)}: 39{,}821.3$$
$$1s \text{ (triplet)}: 20{,}474.5$$

The basic term is thus seen to be the $1S$ term, which, as we explained in the case of sodium, is a 3_1 orbit. This is, therefore, the orbit occupied by the twelfth electron.

The spectrum of *ionized* magnesium, Mg_{II}, consists of a complete system of doublets, similar to the sodium spectrum. The three lowest terms are

$$1\sigma: 121{,}267$$
$$1\pi: 85{,}506$$
$$2\delta: 49{,}777$$

The basic term is, again, the 1σ (or the $1S$, if we disregard the doublet nature of the spectrum). This spectrum is produced by the binding of the eleventh electron, which, therefore, finally reaches a 3_1 orbit..

From a study of the spectrum of Mg_I and of Mg_{II}, we conclude, therefore, that the eleventh and the twelfth electrons of magnesium revolve in 3_1 orbits.

Aluminum ($Z = 13$) yields an arc spectrum of doublets. Here the basic term is 1π:

$$1\pi_1: 48{,}168$$
$$1\sigma: 22{,}933$$

Just as the lowest π term in sodium (Na_I) corresponds to a 3_2 orbit, so the lowest π term in Al_I corresponds to a 3_2 orbit. But this orbit has a lower energy value (larger wave number) than the 1σ term. We conclude, therefore, that the thirteenth electron in Al revolves in the basic orbit 3_2. The $1S$ orbit, however, is the basic orbit in Al_{III}, as is shown by the following data from Bowen and Millikan.[1]

$$Al_{III}\ 1s: = 229{,}455$$
$$1p_1: = 175{,}536$$

This corresponds to a 3_1 orbit. Similarly, the basic term in Al_{II} is a $1s$ term, and the basic orbit a 3_1 orbit. In aluminum,

[1] *Phys. Rev.*, vol. 25, p. 295 (1925).

therefore, the eleventh and twelfth electrons occupy 3_1 orbits, while the thirteenth electron occupies a 3_2 orbit.

Boron ($Z = 5$), in Period II of the periodic table, corresponds to aluminum ($Z = 13$), in Period III. The thirteenth electron of aluminum, which, as we have seen, occupies a 3_2 orbit, is analogous to the fifth electron of boron. By analogy, we infer that the fifth electron of boron occupies a 2_2 orbit. Similarly, we may infer that the fourth electron of beryllium (analogous to the twelfth of magnesium) occupies a 2_1 orbit. We may guess, subject to check by spectroscopic data, that the last-added electron in each of the remaining elements of Period II of the periodic table, namely, C, N, O, F, and Ne, occupies a 2_2 orbit, since we have seen that the last-added electron, *i.e.*, the eleventh, in Na, the first element in Period III, occupies a 3_1 orbit.

The above example will serve to illustrate very briefly the methods and some of the fundamental principles employed in ascertaining the distribution of electrons in orbits.

6. Inner Quantum Numbers.—As was pointed out in Chap. X, Sec. 13, the characterization of spectral terms by the two quantum numbers n (total) and k (azimuthal) has been found insufficient to account for the observed spectroscopic facts. It was found necessary to introduce a third quantum number—the *inner* quantum number j. In the Russell-Saunders notation of spectroscopy (see Chap. X, Sec. 13), the azimuthal quantum number is implied in the (capital) letter used to designate the term, and the inner quantum number is appended as a subscript, thus: P_3 designates a term with azimuthal quantum number k equal to n ($P \equiv 2$) and inner quantum number 3.

Irrespective of any atom model, the spectroscopic *terms* are *observed* physical quantities. Until we attempt to interpret the terms in the light of some atomic mechanism, we may, if we choose, regard the various quantum numbers n, j, and k as playing the part of a mnemonic notation to assist in classifying and in correlating the observed data. When, however, we set up an atom model and attempt to describe the observed phenomena in terms of its properties, these quantum numbers must take on a physical meaning. In terms of the Bohr atom model, the total quantum number n and the azimuthal quantum number k are definitely related to the orbits. The diameter of the orbit—major axis in case of an elliptical orbit—is determined by n. The shape, *i.e.*, eccentricity for a given value of n, is

determined by k. We may think of the inner quantum number j as determining the *orientation* of an orbit with respect to the orbits occupied by the other electrons of the atom. This is equivalent to assuming that there is some "preferential" axis associated with an atom about which its total angular momentum may be measured and that the inner quantum number of an orbit determines the inclination of the orbit to this axis. This inclination is determined by the rules of quantization in much the same way as we have quantized angular momentum.

We have seen that the angular momentum p_ϕ possessed by an electron in its orbital motion around a nucleus is an integer multiple k of the quantity $h/2\pi$, where k is the *azimuthal* quantum number, *i.e.* (see equation (52), Chap. X),

$$p_\phi = k\frac{h}{2\pi} \qquad [(52), \text{Chap. X}]$$

Since p_ϕ is a vector, we may represent it by a line of length k (which is porportional to p_ϕ) drawn perpendicular to the plane of the orbit. If there are 2 electrons in orbital motion around a nucleus, the resultant angular momentum of the system is the *vector* sum of the two individual momenta. If, for example, these two orbits have the same value of k and are coplanar *but oppositely directed*, this vector sum is zero; it is, however, $2k \cdot h/2\pi$ if the 2 electrons revolve in the same direction; it is $\sqrt{2}k \cdot h/2\pi$ if the orbits are inclined at $\pi/2$ to each other. In general, if there are n electrons in orbital motion around a nucleus, the total angular momentum—call it P_ϕ—of the entire system is the vector sum of the individual momenta p_ϕ. These n orbits may be inclined to each other in various ways, so that, even though the individual momenta p_ϕ do not change, P_ϕ may have different values for the various possible configurations. According to the quantum rules, however, only those values of P_ϕ are permissible for which

$$P_\phi = j \cdot \frac{h}{2\pi}$$

where j is an integer (or a half-integer) and is the inner quantum number.

Applying this concept to an orbit exterior to the *core* of an atom, which, we will assume, has a fixed angular momentum, we, in effect, quantize the inclination of the plane of the orbit with respect to the axis about which the angular momentum of the core is measured. Just as the angular momentum p_ϕ is restricted

to a few values determined by the values of k, so the inclination of the orbit to the axis of the core is restricted to a few angles determined by the values of j. It is generally assumed that the total angular momentum of the electrons which form a closed group, such as the 2 electrons in the 2_1 orbits of lithium, is zero. This means that the total angular momentum of the atoms of the inert gases, which, presumably, are made up *entirely* of closed groups, is zero.

The effect of the introduction of the inner quantum numbers, which play a very important role in the quantum theory of the Zeeman and the Stark effects, is to subdivide still further the types of orbits normally occupied by electrons in atoms. In what has been said above, we have considered only subdivisions designated by the azimuthal quantum number k, that is, 3_2, 4_1 . . . or, in general, n_k orbits. Orbits of a *given* n_k are subdivided, except when $k = 1$, into two groups by the use of the inner quantum number j, which is added as a second subscript, thus: n_{kj} and $n_{kj'}$. There are two kinds of 2_2 orbits—2_{21} and 2_{22}—the *second* subscripts $_1$ and $_2$ being the inner quantum numbers j and j' of the orbits. Of orbits which have total quantum number 2 there are *three* kinds—2_{11}, 2_{21}, and 2_{22}. For total quantum number 3, there are five kinds—3_{11}, 3_{21}, 3_{22}, 3_{32}, 3_{33}. This subdivision apparently finds confirmation in X-ray spectra.

Table VI shows the number and the designation of orbits for various values of the total quantum number n. (In X-ray terminology, orbits characterized by the total quantum numbers 1, 2, 3 . . . are designated by the respective letters, K, L, M . . . These are included in the table for comparison and for future use.)

TABLE VI

	K	L	M	N	O
n	1	2	3	4	5
k	1	1 2 2	1 2 2 3 3	1 2 2 3 3 4 4	1 2 2 3 3 4 . . .
j	1	1 1 2	1 1 2 2 3	1 1 2 2 3 3 4	1 1 2 2 3 3 . . .

It would take us too far afield to discuss the methods used in subdividing the electrons of an n_k group into the two groups n_{kj}

and $n_{kj'}$. The results of such an analysis will be referred to in the next section. Reference, however, may be made to the *rule* that the total (maximum) number of electrons in a completed or filled n_{kj} group is $2j$. The maximum number of electrons which can occupy the several orbits given in Table VI is found by multiplying by two the values of j given in the bottom row of the same table. The total number of electrons in complete groups characterized by a quantum number n is the sum of the numbers in each of the subgroups. Thus, the total number of electrons required to complete the orbits for $n = 2$ is $2 + 2 + 4 = 8$, which is the number of electrons in the outer shell of neon, in agreement with the conclusions from chemical data. For $n = 3$, the number of electrons required is $2 + 2 + 4 + 4 + 6 = 18$.

7. Complete Distribution Schemes for All Elements.—Guided, in part, by spectroscopic data of the kind above mentioned and, in part, by further generalizations based on theoretical studies, complete orbital schemes for the various elements have been worked out. For details, we must refer the reader to original articles or to more extensive treatises. McLennan, Lay, and Smith[1] give a set of "rules" on the basis of which they have prepared a table showing the proposed distribution in orbits of the electrons of each of the 92 elements. Among these rules, the following are readily comprehended from what we have said above:

"If the total maximum number of electrons that can occupy an orbit type characterized by the same total and azimuthal quantum numbers n and k, be N, the number N is given by $N = 2(2k - 1)$." For 1_1, 2_1, 3_1 . . . orbits, $k = 1$ and, therefore, $N = 2$. This agrees with the conclusion mentioned above that 1_1 orbits of lithium and of all following elements contain 2 electrons. We saw, also, that there are 2 electrons in 2_1 orbits of beryllium and succeeding elements. Similarly, in aluminum, the 3_1 orbits have 2 electrons. For 2_2, 3_2, 4_2 . . . orbits, $k = 2$, and, hence, $N = 6$. We saw that with boron ($Z = 5$) the fifth electron occupies a 2_2 orbit and that succeeding elements of Period II have all but their first 4 electrons in 2_2 orbits. Neon ($Z = 10$) has, therefore, 6 electrons in 2_2 orbits. For 3_3, 4_3 . . . orbits, $k = 3$ and $N = 10$.

"No two electrons can occupy identical orbits." There may be, for example, a maximum of 6 electrons in 2_2 orbits, but

[1] *Proc. Roy. Soc.* (London), A, vol. 112, p. 77 (1926).

these six 2_2 orbits have different *space* orientations within the atom.

There is, also, a "rule" that, in the process of capturing successive electrons to make a neutral atom, electrons already captured are not shifted into new orbits by succeeding captures.

A table has been prepared by P. D. Foote based on the work of Bohr,[1] Stoner,[2] Main Smith,[3] Pauli,[4] Heisenberg,[5] Sommerfeld,[6] Hund,[7] and others, which shows the proposed distribution of electrons in the various (n_{kj}) groups. This table is reproduced as Appendix II.

At first glance, such tables as these which purport to show the distribution of electrons in orbits may seem very speculative and highly artificial. The fact, however, that the proposed distribution receives confirmation from quite diverse fields in physics and chemistry, and, more important, the usefulness of these tables and the general underlying theories in predicting new phenomena[8] are indicative of a fundamental "something," which—though our concrete picture of the atom may be, and probably is, quite incorrect—is of far-reaching importance.

[1] "Theory of Spectra and Atomic Constitution," Cambridge University Press (1922).

[2] *Phil. Mag.*, vol. 48, p. 719 (1924).

[3] "Chemistry and Atomic Structure," D. Van Nostrand Company (1924).

[4] *Zeit. für Physik*, vol. 31, p. 765 (1925).

[5] *Zeit. für Physik*, vol. 32, p. 841 (1925).

[6] "*Atombau und Spektrallinien*," *Friedr. Vieweg & Sohn* (1924).

[7] *Zeit. für Physik*, vol. 33, p. 335 (1925).

[8] Witness the discovery of the element hafnium ($Z = 72$) by Coster and Hevesy (*Nature*, vol. 111, p. 79 *et seq*, 1923) as a result of the prediction by Bohr that this missing element should be analogous to zirconium, instead of belonging to the rare-earth group.

CHAPTER XII

X-RAYS

There is probably no subject in all science which better illustrates the importance *to the entire world* of research in pure science, than do X-rays. Within 3 months after Roentgen's fortuitous discovery, X-rays were being put to practical use in a hospital in Vienna in connection with surgical operations. The use of this new aid to surgery soon spread rapidly. Since Roentgen's time, X-rays have completely revolutionized certain phases of medical practice. Had Roentgen deliberately set about to discover some means of assisting surgeons in reducing fractures, *it is almost certain that he would never have been working with the evacuated tubes, induction coils, and the like, which led to his famous discovery.*

In other fields of applied science, both biological and physical, uses have been found for X-rays, which approximate in importance their use in medicine. One may mention, for example, the study of the crystal structure of materials; "industrial diagnosis," such as the search for possible defects in the materials of engineering; the analysis of coal; the detection of artificial gems; the study of old paintings; the study of the structure of rubber; and many other uses.

But transcending these uses in applied science are the applications which are made of X-rays to such problems as the atomic and the molecular structure of matter and the mechanism of the interaction of radiation with matter. X-rays provide us with a kind of supermicroscope, by means of which we can "see" not only atoms and their arrangement in crystals but also even the interior of the atom itself. Roentgen's discovery must be ranked with the most important scientific discoveries of all time.

In this chapter, we shall give a brief account of the development and the present status of X-rays, with particular reference to their application to some of the fundamental problems of physics.

1. Roentgen's Discovery.—In the autumn of 1895, Wilhelm Konrad Roentgen, professor of physics at Würzburg, was study-

ing that fascinating phenomenon, the discharge of electricity through rarefied gases. A large induction coil was connected to a highly evacuated tube (Fig. 113) the cathode *C* being at one end and the anode *A* at the side. The tube was covered "with a somewhat closely fitting mantle of thin black cardboard."[1] With the apparatus in a completely darkened room, he made the quite accidental observation that "a paper screen washed with barium-platino-cyanide lights up brilliantly and fluoresceses equally well whether the treated side or the other be turned toward the discharge tube."[1] The fluorescence was observable 2 meters away from the apparatus. Roentgen soon convinced himself that the agency which caused the fluorescence originated at that point in the discharge tube where the glass walls were struck by the cathode stream in the tube.

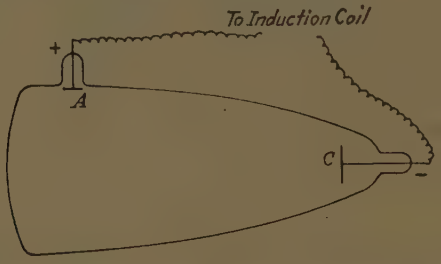


FIG. 113.—Schematic representation of the tube with which Roentgen discovered X-rays.

Realizing the importance of his discovery, Roentgen at once proceeded to study the properties of these new rays—the unknown nature of which he indicated by calling them "X-rays." In his first communications,[2] he recorded, among others, the following observations:

1. *All substances are more or less transparent to X-rays.* For example, the fluorescent screen lighted up when a bound volume of 1,000 pages was held between it and the tube. Wood 2 to 3 cm. thick was very transparent. Aluminum 15 mm. thick "weakens the effect considerably, though it does not entirely destroy the fluorescence." Lead glass was quite opaque. Other glass of the same thickness was much more transparent. "If

[1] Quotations from papers by ROENTGEN: *Electrician* (London), vol. 36, p. 415 (Jan. 24, 1896).

[2] In addition to the paper mentioned above, see Roentgen's second communication: *Electrician*, vol. 36, p. 850 (Apr. 24, 1896).

the hand is held between the discharge tube and the screen the dark shadow of the bones is visible within the slightly dark shadow of the hand." The opacity of a substance depends not only upon its density but also upon some other property. For example, a sheet of platinum 0.018 mm. thick had the same opacity as 3.5 mm. of aluminum. The ratio of the thickness of these two sheets is about 1:200. The ratio of the densities of the materials is about 8:1.

2. Many other substances besides barium-platino-cyanide fluoresce—phosphorus, calcium compounds, uranium glass, rock salt, etc.

3. Photographic dry plates and films "show themselves susceptible to X-rays." Hence, photography provided a valuable method of studying the effects of X-rays.

4. The rays are neither reflected nor refracted. Hence, "X-rays cannot be concentrated by lenses."

5. X-rays, unlike cathode rays, are not deflected by a magnetic field. They travel in straight lines, as Roentgen showed by "pinhole" photographs.

6. X-rays discharge electrified bodies,[1] whether the electrification be positive or negative.

7. X-rays are generated when the cathode rays of the discharge tube strike *any* solid body, such as aluminum or platinum. A heavier element, such as platinum, however, is much more efficient as a generator of X-rays than is a lighter element, such as aluminum. Roentgen, in the second paper, describes

> . . . a discharge apparatus in which a concave mirror of aluminum acted as cathode and a sheet of platinum as anode, the platinum being at an angle of 45 degrees to the axis of the mirror and at the center of curvature.

This form of X-ray tube was the prototype of practically all X-ray tubes until the introduction of the Coolidge tubes, about 1913.

In his first communication, Roentgen, arguing from the fact that these new rays "behave in quite a different manner to any infra-red, visible or ultra-violet rays hitherto known," asked the

[1] This property of X-rays was independently discovered by Sir J. J. Thomson (see letter to *Electrician* (Feb. 4, 1896)). Thomson pointed out that this phenomenon provides a method of studying X-rays much more delicate and expeditious than the photographic plate or the fluorescent screen and, further, that it yields quantitative measurements.

question, "May not these new rays be due to longitudinal vibrations in the ether?"

2. Some Early Experiments and Theories.—Roentgen's discovery excited intense interest throughout the entire scientific world. His experiments were repeated, and extended, in very many laboratories in both America and Europe. The scientific journals, during the year 1896, were filled with letters and short articles describing new experiments or confirmations of observations previously made.[1] These experiments were facilitated by the fact that during the years immediately preceding Roentgen's discovery the discharge of electricity through rarefied gases had been a very popular topic for study by physicists. Equipment similar to Roentgen's was, therefore, in operation in many research laboratories. Further, considerable impetus was given to research in this field because of its important practical applications in surgery and elsewhere.

As was to be expected, many of these early experiments brought forth conflicting evidence, and most of them were the result of gropings in the dark in the absence of any guiding theory. Nevertheless, particularly from a historical standpoint, these early experiments are not without interest. By way of illustration, we shall summarize a few of them—making no attempt, however, to give a complete survey.

(*a*) *Sources of X-rays.*—Tubes for the production of X-rays very soon became more or less standardized along lines suggested by Roentgen, as mentioned in the previous section. A tube similar to Roentgen's, in which the cathode rays from a curved cathode were brought to a focus onto a piece of platinum inclined at 30 to 40 degrees to the direction of the rays, was described by S. P. Thompson.[2] Figure 114(*a*) shows, schematically, such a tube. *C* is the curved cathode, the cathode rays from which converge onto, or are "focused" onto, the anode *A*, which is a sheet of metal such as platinum, inclined at 45 degrees to the axis of the cathode stream. The potential is supplied to the tube by an induction coil, electrostatic machine, or other source of sufficiently high potential. In this type of tube, known as the "gas" tube, it is essential that the gas pressure within the tube

[1] See, for example, *Science*, vol. 3 (1896), which contains translations of Roentgen's papers and numerous short articles with X-ray photographs. The *Beiblatter zu der Ann. Physik* for 1896 contains 400 titles on X-rays!

[2] *Compt. rend.*, vol. 122, p. 807 (1896).

be maintained at the desired value. Various ingenious devices were introduced for accomplishing this. These gas tubes were practically the only source of X-rays up to the introduction of the Coolidge tube.

The Coolidge tube,[1] introduced by Dr. W. D. Coolidge, in 1913, differs from the gas tube in two very important particulars: (1) In the gas tube, the electrons of the cathode stream are supplied as a result of the ionization of the residual gas in the tube. In the Coolidge tube (Fig. 114(*b*)), the electrons are supplied by the thermionic emission from a flat, spirally wound tungsten filament F heated by a small battery B or by a low-

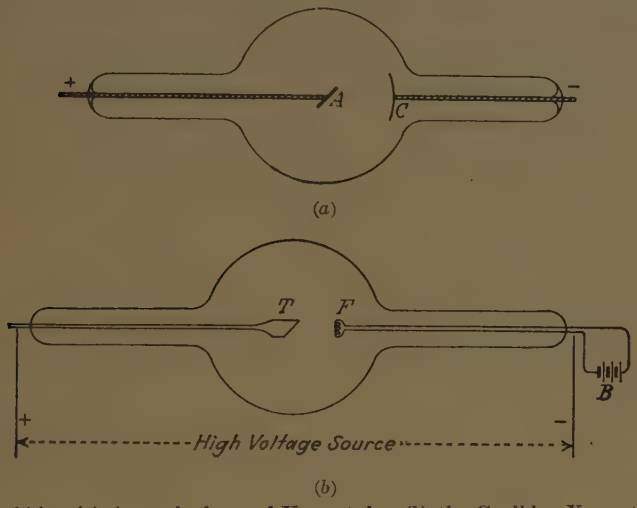


FIG. 114.—(*a*) An early form of X-ray tube; (*b*) the Coolidge X-ray tube.

voltage transformer. (2) It is, therefore, possible to dispense entirely with the gas in the tube—the Coolidge tube is evacuated to the highest attainable vacuum. One very important advantage of the Coolidge X-ray tube over the gas tube is the possibility of controlling the current through the tube independently of the voltage applied to the tube. In the Coolidge tube, the current can be adjusted to any desired value, irrespective, within limits, of the applied voltage. In the gas tube, current, applied voltage, and gas pressure are more or less interdependent. The controllable features of the Coolidge tube have greatly facilitated research in X-rays, particularly in those

[1] *Phys. Rev.*, vol. 2, p. 409 (1913).

investigations which require high precision in the measurement of the energy in an X-ray beam.

(*b*) *Improvements in Photographic Methods.*—The use of X-ray photography in surgical work made it desirable to shorten exposures as much as possible. The application of fluorescent—or, as we now say, intensifying—screens to increase the effective speed of photographic emulsions was independently made by numerous investigators. That the intensity of the photographic image was greatly increased by painting the *glass* side of the photographic plate with phosphorescent zinc sulphide was discovered by C. Henry.[1] Basilewski[2] modified this procedure by coating a sheet of paper with the fluorescent material and laying the sheet face down on the photographic emulsion. Buguet[3] used a sheet of lead instead of fluorescing material. Edison[4] discovered that calcium tungstate properly crystallized fluoresces brilliantly. This was later used for intensifying screens. Elihu Thompson[5] made the very important discovery that two X-ray photographs of an object taken at slightly different directions and viewed by aid of a stereoscope would stand out in high relief.

(*c*) *Ionization Measurements.*—Use was at once made of the discovery independently announced by Thomson and by Roentgen, that X-rays discharge charged bodies and that the rate of discharge is a measure of the intensity of the rays. Perrin[6] showed that this discharging action of the rays is apparently due to the fact that the rays make the air surrounding the charged body conducting. It was suggested that the air molecules are broken up by the rays into positively and negatively charged ions. This suggestion was in harmony with the observation of Roentgen[7] that under the action of X-rays charged bodies placed in a vacuum lose their charge very much more slowly than they do in air. Further, Villari[8] showed that "Roentgenized" air preserves its property of discharging an electroscope even after passing through a tube 10 meters long. He also showed that the

[1] *Compt. rend.*, vol. 122, p. 312 (1896).
[2] *Compt. rend.*, vol. 122, p. 720 (1896).
[3] *Compt. rend.*, vol. 122, p. 702 (1896).
[4] *Electrician*, vol. 36, p. 702 (1896).
[5] *Electrician*, vol. 36, p. 661 (1896).
[6] *Compt. rend.*, vol. 122, p. 186 (1896).
[7] *Electrician*, vol. 36, p. 850 (1896).
[8] *Compt. rend.*, vol. 123, pp. 418, 446 (1896).

discharging action in a gas at a given pressure depends on the nature of the gas. The following were found increasingly active in the order given: H, CO, air, CO_2, ether vapor, CS_2. Benoist and Hurmuzescu[1] showed that, for a given gas, the discharging action increases rapidly with density.

This property of X-rays, in making a gas through which they pass electrically conducting, has been used from the very first as a quantitative means of measuring the intensity of an X-ray beam. At first, the rate of discharge of a charged electroscope was used, the motion of the leaves being observed by a low-power microscope. Later, an auxiliary device, known as an "ionization chamber," was introduced. This is shown schematically in Fig. 115. *C* is a metal tube several centimeters in diameter, from 20 to 100 cm. long, and closed at both ends except for an

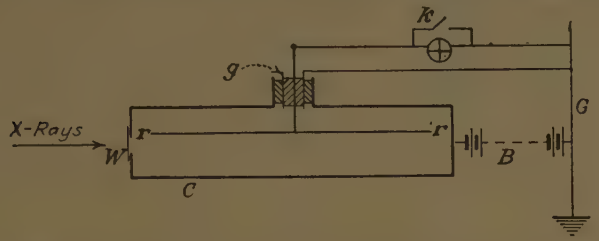


FIG. 115.—The ionization chamber used for measuring electrically the intensity of a beam of X-rays.

opening or "window" *W*, over which may be placed a thin sheet of aluminum for admitting the X-rays. A rod *rr* suitably supported by *good* insulating material, such as amber or quartz, is connected to an electrometer. An electric field is maintained between the rod *rr* and the cylinder *C* by a battery *B*, of several hundred volts, one end of which is connected to the ground wire *G*. An earthed guard ring *g* prevents leakage from the cylinder to the rod *rr*. In accordance with the observations of Villari, the cylinder may be filled with a heavy gas to make the arrangement more sensitive.

When X-rays enter the window *W*, the gas within the cylinder is made conducting, and on account of the electric field between the cylinder and the rod the latter acquires a charge at a rate which can be measured by the electrometer, which rate is determined by, and is, therefore, a measure of, the intensity of the X-ray beam.

[1] *Compt. rend.*, vol. 122, p. 926 (1896).

(*d*) *The Absorption of X-rays.*—Roentgen's initial observation, that the relative opacity of materials to X-rays depends not alone upon density, was early confirmed. Bleunard and Lablesse,[1] Novak and Sule,[2] Benoist,[3] and Marangoni[4] all came, independently, to the conclusion that the opacity of a material to X-rays depends upon its atomic weight. Buguet[5] showed that the beam of rays from an X-ray tube is not homogeneous, since the opacity of a given material to the rays depends upon the thickness of material previously traversed by the beam. This showed that the quality of a beam of X-rays could be altered by varying the thickness of the material through which the beam is made to pass.

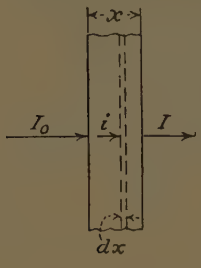


FIG. 116.

For many years, the absorbability of X-rays in some standard material such as aluminum was the only measure of the *quality* of the beam. Rays were called "hard rays" or "soft rays," according as they more readily passed through, or were more readily absorbed by, aluminum.

We shall have frequent occasion to make quantitative reference to the absorption of X-rays. It will be desirable, therefore, to derive the general formula for the absorption of any type of radiation as it passes through matter. Let a beam of radiation of intensity I_0 be normally incident onto a slab (Fig. 116) of absorbing material of thickness x; and let I be the intensity of the emergent beam. Let i be the intensity of the beam after it has penetrated into the slab as far as the thin layer of thickness dx; and let di be the *diminution* in intensity in passing through this thin layer dx. Then, so long as di/i is very small,

$$\frac{di}{i} = -\mu dx \qquad (1)$$

where μ is a proportionality factor called the *coefficient of absorption*. Integrating equation (1) from one face of the slab to the other, we have

$$\int_{I_0}^{I} \frac{di}{i} = -\int_0^x \mu dx$$

$$\therefore \log \frac{I}{I_0} = -\mu x$$

[1] *Compt. rend.*, vol. 122, p. 723 (1896).
[2] *Zeit. für Phys. Chem.*, vol. 19, p. 489 (1896).
[3] *Compt. rend.*, vol. 122, p. 146 (1896).
[4] *Rend. Acc. Linc.*, vol. 5, p. 403 (1896).
[5] *Compt. rend.*, vol. 125, p. 398 (1897).

or

$$I = I_0 e^{-\mu x} \tag{2}$$

By measuring I, I_0, and x, one may compute μ. If we are measuring the coefficient of absorption of X-rays, I_0 and I may be measured by the ionization chamber mentioned above.

In deriving equation (2), we are not concerned with what ultimately becomes of the radiation which is *removed* from the incident beam. We are concerned *only* with the fact that as a result of the passage through the slab of material the intensity of the radiation has been reduced from I_0 to I.

In discussions of the absorption of X-rays, a quantity known as the *mass* absorption coefficient is frequently used. Let the exponent in equation (2) be both multiplied and divided by ρ, the density of the slab. We then have

$$I = I_0 e^{-\frac{\mu}{\rho} \cdot \rho x} \tag{3}$$

The quantity μ/ρ is called the *mass* absorption coefficient; ρx is, obviously, the mass of a portion of the slab 1 sq. cm. in cross-section and x cm. thick.

(*e*) *Scattering.*—That X-rays are scattered or diffused, as is light by fog particles, was early recognized. In an attempt to dis-

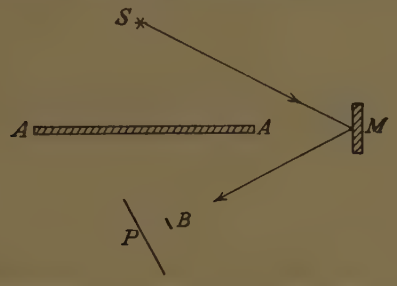


FIG. 117.—The arrangement of Imbert and Bertin-Sans showing "pseudo" reflection (scattering) from the mirror M.

cover the reflection of X-rays, Imbert and Bertin-Sans[1] arranged apparatus, as shown diagrammatically in Fig. 117. Between the source S of the rays and the photographic plate P was placed a thick copper screen AA. A plane mirror M was so positioned that a beam of rays, if reflected, would pass to the photographic plate P, on which would appear an image or shadow of an obstacle B. Such a shadow was obtained *irrespective of the angular posi-*

[1] *Compt. rend.*, vol. 122, p. 524 (1896).

tion of the mirror M. Indeed, a plate of paraffin was just as effective as the mirror *M*, from which fact Imbert and Bertin-Sans concluded that the rays were *diffused* or *scattered* from *M*, rather than reflected, and that probably the rays were *waves of very small wave length*, too small to be reflected from (artificially) polished surfaces.

Righi[1] showed that an electroscope *E*, although placed in the "shadow" of a lead screen *Pb* (Fig. 118) would be discharged by the action of X-rays emitted by the source *S*. This effect was later shown to be due to the scattering effect of the air in the neighborhood of the screen.

An important observation was made by Winkelmann and Straubel.[2] A beam of X-rays was passed through a photographic plate *P* (Fig. 119), the emulsion being on the rear side. Behind

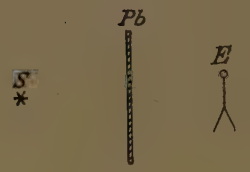


FIG. 118.

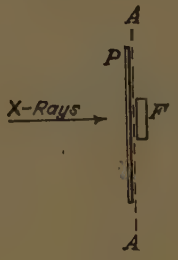


FIG. 119.

a part of the plate was placed a piece of fluorspar *F*. On developing the plate, it was found that the film was much denser in the neighborhood of *F*, as if *F* had reflected the rays. An observation of this kind had been made by Roentgen. But Winkelmann and Straubel showed that the phenomenon was not one of true reflection, for they repeated the experiment with a thin sheet of paper *AA* between *F* and *P* and found that the intensifying action of *F* was almost entirely destroyed, although the paper was very transparent to the *incident* beam. From this, they concluded that the *quality* of the rays had been altered by the spar in such a way as to make the beam of rays returned by *F* more absorbable in paper than was the original beam. In other words, the primary rays, incident onto the spar, had been transformed into *characteristic* "spar" rays.

[1] *Rend. Acc. Linc.* (1896).

[2] *Zeit. für Naturw.*, vol. 30 (1896).

(*f*) *Refraction and Diffraction.*—Roentgen, in his first papers, reported that he had failed to find either refraction or diffraction of X-rays. Because of the importance of this observation, more diligent search for evidences of these phenomena was undertaken. Gouy[1] had observed that X-rays emitted in different angular directions from a plane platinum target were of nearly the same intensity down almost to grazing incidence. By taking rays, from a plane target, at nearly grazing incidence, a very narrow, and quite intense, line source of X-rays is thus available. Such a line source was used to get a shadow of a fine platinum wire on a photographic plate, a prism being placed in the path of part of the rays in such a way that if the rays were *refracted* by the prism, the shadow of the wire would be "broken." The shadow was sharp and continuous, showing no measurable refraction. Gouy estimated that the index of refraction could not be greater than 1.000005.

Gouy[2] and, independently, Forum[3] searched for evidences of diffraction, with negative results. They concluded that if X-rays are waves, subject to the same laws as light, their wave length cannot be greater than about 10×10^{-7} cm.

(*g*) *Early Theories.*—The experimental conclusions from these early experiments were, substantially, as follows:

1. X-rays are produced when the cathode stream in a highly evacuated discharge tube falls upon a solid obstacle.
2. These rays cause fluorescence, affect a photographic plate, and ionize air—just as does ultra-violet light.
3. But, unlike ultra-violet light, X-rays are neither reflected, refracted, nor diffracted; and they readily penetrate matter opaque to ultra-violet light.
4. Air and other gases, however, as well as solid bodies, scatter X-rays, much after the manner of the action of fog particles upon light.

What were these new rays?

Roentgen's early suggestion that perhaps X-rays might be longitudinal ether waves was not well received. The weight of opinion inclined to the view that X-rays are very short ultra-violet waves, since X-rays exhibit so many of the properties of

[1] *Compt. rend,* vol. 122, p. 1197 (1896).
[2] *Compt. rend.,* vol. 123, p. 43 (1896).
[3] *Ann. Physik,* vol. 59, p. 350 (1896).

ultra-violet light. It was pointed out by Maltezos[1] that the Helmholtz dispersion formula

$$n^2 = 1 + C\lambda^2 + \cdots$$

where n is the index of refraction and C is a constant, predicts that $n \doteq 1$ as $\lambda \doteq 0$, which is in agreement with the assumption that X-rays are very short waves, of an order of magnitude probably not exceeding 10^{-7} cm. This same theory would explain the absence of reflection and diffraction.

A little later, Haga and Wind[2] carried out a series of experiments in an attempt to detect the diffraction of X-rays. With wedge-shaped slits only a few thousandths of a millimeter wide, they observed evidences of a slight widening of the image on the photographic plate, from which they deduced that the probable wave length of the rays must be of the order of 10^{-8} cm. This result—although confirmed qualitatively by experiments over 2 decades later—was not given much weight, partly because of the smallness of the effect, partly because, in the meantime, the classical "ether pulse" theory of X-rays had been developed by Schuster,[3] Wiechert,[4] Stokes,[5] Sir J. J. Thomson,[6] and others. We shall discuss this theory briefly in the next section.

3. The Ether-pulse Theory of X-rays. (*a*) *The Production of X-rays.*—Theories concerning the mechanism of the cathode-ray discharge were beginning to take definite form as a result of experiments in this field covering a period of many years. These experiments culminated in the discovery of the electron, by Sir J. J. Thomson, in 1897. It then became clear that the cathode stream in a discharge tube consists of swiftly moving electrons. If these electrons, moving with high velocity and carrying, as they do, a negative charge, be suddenly brought to rest by colliding with a solid obstacle—the glass walls of the discharge tube or a piece of metal deliberately put in the path of the rays—they must experience, for a brief interval, a very large negative acceleration. According to the electromagnetic theory, such an accelerated body must radiate energy. The sudden stopping

[1] *Compt. rend.*, vol. 122, pp. 1115, 1474, 1533 (1896).
[2] *Ann. Physik*, vol. 68, p. 884 (1899).
[3] *Nature*, p. 268 (Jan. 23, 1896).
[4] *Ann. Physik*, vol. 59, p. 321 (1896).
[5] STOKES: The Wilde Lecture (1897).
[6] *Phil. Mag.*, vol. 45, p. 172 (1898).

of each electron as it collides with the target of the X-ray tube results in the emission of an electromagnetic disturbance or pulse frequently called an "ether pulse." On this theory, the X-rays emitted by a target consist of a very rapid succession of such pulses, coming at random intervals. It was shown by Stoney[1] that such a stream of pulses could be analyzed into wave trains, the components of shorter wave length being the more abundant the greater the velocity of the electrons which are brought to rest by the target. Stoney showed that matter should, in general, be more transparent to the shorter waves than to the longer waves. The hard, or penetrating, X-rays should, therefore, be produced by high-velocity electrons, which, in turn, are produced by high voltages applied to the X-ray tube. Qualitatively, this picture of the mechanism of the production of X-rays seemed to be in agreement with the experimental facts.

In Chap. V, we discussed some fundamental principles concerning accelerated charges, which are directly applicable to the ether-pulse theory of X-rays. It was shown that when a charge e moving with velocity v is brought to rest in such a time that a pulse of thickness δ is emitted, the total energy W radiated is given by (see equation (34), Chap. V).

$$W = \frac{2}{3}\frac{e^2v^2}{c^2\delta} \qquad [(34), \text{Chap. V}]$$

This energy W which is radiated by the stopping of the electron was shown to be a fraction

$$\frac{2a}{\delta}$$

of the *total* kinetic energy of the moving charge (see equation (37), Chap. V), where a is the diameter of the electron. The fraction of its energy which is radiated when the electron is stopped is, therefore, inversely proportional to δ, the thickness of the pulse. Now, the thickness of the pulse is directly proportional to the time required to stop the electron (see equation (25), Chap. V). And it is reasonable to assume that an electron moving with given velocity will be stopped more suddenly when colliding with a heavy atom than with a lighter one. Other things being equal, therefore, a more intense X-ray beam should be produced when a heavy material such as platinum is used as the target in an X-ray tube than when a lighter metal such as

[1] *Phil. Mag.*, vol. 45, p. 532; vol. 46, p. 253 (1898).

aluminum is employed. This is in agreement with Roentgen's observation, noted above. In other words, heavy targets are more efficient sources of X-rays than are lighter ones.

(*b*) *The Scattering of X-rays.*—Mention was made above (see Sec. 2(*e*)) of the experiments of Imbert and Bertin-Sans, who showed that X-rays are *scattered* when they pass through matter. This phenomenon of the scattering of X-rays has played a very important part in the theories of modern physics and has been the object of many researches, both theoretical and experimental. The ether-pulse theory of X-rays, together with the concept of the electrical nature of matter, which was firmly established by the discovery of the electron, formed the basis of a theory of scattering proposed by Sir J. J. Thomson.[1]

Let us consider that a swiftly moving electron in an X-ray tube is suddenly brought to rest by colliding with a target at

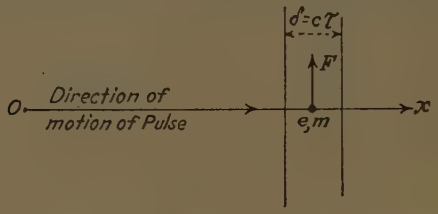


FIG. 120.—The force acting on an electron during the passage of an ether pulse.

point O (Fig. 120). As a result of this collision, a spherical pulse of thickness $\delta = c\tau$, where τ is the time required to stop the electron, will spread out radially from O. This pulse, as was shown in Chap. V, consists of an electric vector and a magnetic vector at right angles both to each other and to the direction of propagation. Let us consider a point, in the x direction from O, at which is located an electron of charge $-e$ and mass m. As the pulse passes over the electron, the latter will experience a force F given by

$$F = Y \cdot e$$

where Y is the electric vector in the pulse. For simplicity, let us consider that Y is constant throughout the thickness of the pulse. The electron will then be given a *constant* acceleration g given by

$$g = \frac{Ye}{m} \qquad (4)$$

[1] "Conduction of Electricity through Gases," 2d. ed., p. 321.

which acceleration will last for a time τ required for the pulse to pass. As a result of this acceleration, the electron will radiate energy at a rate given by equation (36) of Chap. V, namely,

$$\frac{dW}{dt} = \frac{2}{3}\frac{e^2 g^2}{c^3} \qquad [(36), \text{Chap. V}]$$

Putting into this equation the value of g from equation (4), we have

$$dW = \frac{2}{3}\frac{e^4}{c^3}\frac{Y^2}{m^2}\,dt$$

The total energy W radiated by the electron as a result of the passage of the pulse over it will be

$$W = \frac{2}{3}\frac{e^4}{m^2c^3}\int_0^\tau Y^2 dt \qquad (5)$$

$$= \frac{2}{3}\frac{e^4}{m^2c^3}Y^2\tau \qquad (6)$$

if, as mentioned above, we consider Y constant.[1]

This energy W is radiated as a *secondary* pulse as a result of the passage over the electron of the *primary* pulse. The electron has, therefore, *scattered* some of the energy of the primary pulse. We shall consider presently the *direction* in which this energy is scattered.

[1] This limitation of Y to a constant value throughout the pulse is quite unnecessary. In equation (5), we are concerned with the integral $\int_0^\tau Y^2 dt$. Since the energy per cubic centimeter from point to point in the pulse is proportional to Y^2, the *intensity* of the pulse I is given by

$$I = \frac{1}{4\pi}\int_0^\delta Y^2 d\delta$$

where $d\delta$ is a thin slice of the pulse taken parallel to the surfaces of the pulse. Since $\delta = c\tau$ and, therefore, $d\delta = c\,dt$, it readily follows that

$$I = \frac{c}{4\pi}\int_0^\tau Y^2 dt$$

We then have for W, from equation (5),

$$W = \frac{8\pi}{3}\cdot\frac{e^4}{m^2c^4}I$$

from which equation (9) may be readily deduced.

Let us consider that this scattering electron is simply one of a large number of electrons in a slab of material of thickness dx (Fig. 121) through which the primary pulse passes. And let us assume that *every* electron in the slab scatters exactly the same amount of energy W. Let n be the total number of electrons per cubic centimeter in the slab. Then, ndx is the number of electrons in a portion of the slab 1 sq. cm. in cross-section and dx cm. thick. Each of these ndx electrons removes from the primary beam by the process of scattering an amount of energy W. The total amount of energy dI removed from the beam by 1 sq. cm. of the slab is, obviously,

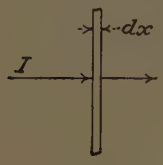


FIG. 121.

$$dI = W \cdot ndx = \frac{2}{3}\frac{e^4}{m^2c^3} nY^2 \tau dx \tag{7}$$

The energy per cubic centimeter in the pulse is given by

$$\frac{Y^2}{4\pi}$$

and the intensity I of the pulse is

$$I = \frac{Y^2}{4\pi}\delta = \frac{Y^2}{4\pi} c\tau \tag{8}$$

where $\delta = c\tau$ is the thickness of the pulse. The *fractional diminution* of energy resulting from the scattering process when the pulse passes through the slab is, therefore, given by

$$\frac{dI}{I} = -\left[\frac{8\pi}{3} \cdot \frac{e^4}{m^2c^4} n\right] dx \tag{9}$$

By analogy with equation (2) for the *absorption* coefficient μ, we may write equation (9) in the form

$$\frac{dI}{I} = -\sigma \cdot dx$$

where σ is the *scattering* coefficient and is given by

$$\sigma \equiv \frac{8\pi}{3}\frac{e^4}{m^2c^4} n \tag{10}$$

As a result of the scattering process, therefore, an incident beam of X-rays of intensity I_0 should, in passing through a slab of material of thickness x containing n (*scattering*) electrons per cubic centimeter, be reduced in intensity to I according to the equation

$$I = I_0 e^{-\sigma x} \tag{11}$$

If, now, we assume that it is only by the scattering process that energy is removed from the incident beam, we can measure σ by measuring I_0, I, and x. In equation (10) for σ all quantities are known except n, the number of scattering electrons per cubic centimeter. By measuring σ, therefore, we may compute n. Barkla[1] was the first to determine, by this method, the number of electrons per cubic centimeter of a scattering material and, from this number, the number of electrons per atom. Barkla found from observations of scattering that for carbon the value of σ/ρ, the *mass* scattering coefficient, is approximately 0.2. In the equation

$$\frac{\sigma}{\rho} = \frac{8\pi}{3}\frac{e^4}{m^2c^4}\frac{n}{\rho} \tag{12}$$

we may set $\sigma/\rho = 0.2$ from Barkla's observation; $e = 4.77 \times 10^{-10}$; $m = 9 \times 10^{-28}$; $c = 3 \times 10^{10}$. We thus find that n/ρ, the number of scattering electrons per gram of carbon, is about 3×10^{23}. The number of atoms of carbon per gram is given by

$$\frac{N}{A} = \frac{6.06 \times 10^{23}}{12} = 5.05 \times 10^{22}$$

where N is Avogadro's number and A is the atomic weight. The number of electrons per *atom* of carbon is, therefore,

$$\frac{n/\rho}{N/A} = \frac{3 \cdot 10^{23}}{5.05 \cdot 10^{22}} = 6 \text{ (approximately)} \tag{13}$$

This was one of the first determinations of the number of electrons per atom, a result which was reached by a straightforward application of classical theory.

(*c*) *Angular Distribution of Scattered X-rays.*—We saw, in Chap. V (equation (30)), that the distribution of intensity over the surface of a pulse emitted when an electron is accelerated is not uniform but is proportional to $\sin^2\theta$, where θ is the angle between the direction of the acceleration and the direction in which the intensity is measured; *i.e.*, the intensity I_θ at the angle θ is given by (see equation (30), Chap. V),

$$I_\theta = \frac{1}{4\pi}\frac{e^2v^2}{c^2R^2\delta}\sin^2\theta \qquad [(30), \text{Chap. V}]$$

[1] *Phil. Mag.*, vol. 28, p. 648 (1911).

where v is the initial velocity of the charge e which is brought to rest, δ is the thickness of the resulting pulse, and R is the distance of the point of observation from the center of the pulse (see Fig. 24). Taking $v = g\tau$, where g is the uniform acceleration which brings the charge to rest in time τ, and $\delta = c\tau$, we can transform equation (30), Chap. V, into

$$I_\theta = \frac{1}{4\pi} \frac{e^2 g^2}{c^3 R^2} \tau \sin^2 \theta \tag{14}$$

which gives I_θ in terms of the acceleration g.

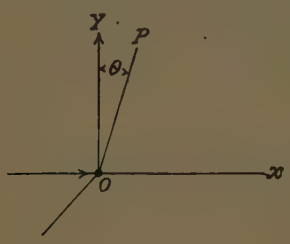


FIG. 122.

Now, let a plane-polarized primary pulse of intensity I and thickness $\delta = c\tau$ proceeding in the x direction pass over an electron at O (Fig. 122), the electric vector in the pulse being Y. The acceleration g_e experienced by the electron will be

$$g_e = \frac{Ye}{m}$$

The intensity I'_θ of the *secondary* pulse in a direction $\theta = \angle POY$ and at a distance R from O will be, according to equation (14),

$$I'_\theta = \frac{1}{4\pi} \frac{e^2}{c^3 R^2} \cdot \frac{Y^2 e^2}{m^2} \tau \sin^2 \theta \tag{15}$$

Since $c\tau = \delta$, and since the intensity of the primary pulse I is

$$I = \frac{1}{4\pi} Y^2 \delta \tag{16}$$

(assuming Y constant throughout the pulse), we have, from equation (15),

$$I'_\theta = I \cdot \frac{e^4}{m^2 c^4} \frac{1}{R^2} \sin^2 \theta \tag{17}$$

That is to say, the intensity I' of the *secondary* pulse is proportional to the intensity of the primary pulse and to $\sin^2 \theta$. The intensity I' is greatest in the xz plane; it is zero in the y direction.

Let us now consider the more general case where the X-ray beam consists not of a single plane-polarized pulse but of a rapid succession of such pulses, the electric vectors of which are distributed at random in the yz plane so that the time average of the components of the electric vector in the y direction is $\overline{Y}$, and in the z direction is $\overline{Z}$. Since the distribution is random

$$\overline{Y} = \overline{Z}$$

Applying an equation of the type of equation (17) to determine the intensity of the scattered beam at some point P in the xy plane (Fig. 123), due to each component Y and Z separately, we have

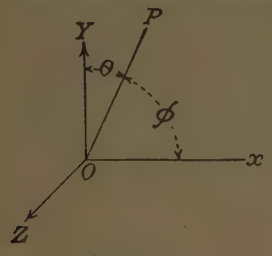


FIG. 123.

$$I'_{\theta,Y} = I_Y \cdot \frac{e^4}{m^2c^4}\frac{1}{R^2}\sin^2\theta$$

$$= I_Y \cdot \frac{e^4}{m^2c^4}\frac{1}{R^2}\cos^2\phi \qquad (18a)$$

$$I'_{\theta,Z} = I_Z \cdot \frac{e^4}{m^2c^4}\frac{1}{R^2}\sin^2\frac{\pi}{2}$$

$$= I_Z \cdot \frac{e^4}{m^2c^4}\frac{1}{R^2} \qquad (18b)$$

since $\angle POz = \pi/2$. Remembering that the intensity I of the primary beam is given by

$$I = I_Y + I_Z$$

and that the intensity of the secondary beam is

$$I'_\theta = I'_{\theta,Y} + I'_{\theta,Z}$$

we have for I'_ϕ, by addition of equations (18),

$$I'_\phi = I\frac{e^4}{m^2c^4} \cdot \frac{1}{R^2}(1 + \cos^2\phi) \qquad (19)$$

where ϕ is the angle which the direction OP makes with the direction of propagation of the X-ray beam. According to equation (19), the intensity of the scattered X-ray beam should be symmetrical about the direction of propagation of the primary beam and, also, forward and backward, about a plane (the yz plane in the figure) passing through the scatterer and perpendicular to the direction of propagation. We shall see, later, that there are found, experimentally, radical departures from this second condition of symmetry. In a later section, we shall return to the question of the scattering of X-rays.

(*d*) *Polarization of X-rays.*—Measurements of the scattering of X-rays yield information concerning polarization. Let a stream of cathode rays, proceeding in the direction zO (Fig. 124) impinge on a target at O. Consider the beam of X-rays proceeding from this target in the direction Ox_1. We shall call this the "primary beam." If we assume that the electrons of the cathode stream are all brought to rest by accelerations in the direction Oz, this primary beam should be plane polarized with the electric vector in the z direction, as indicated by the vector Z. Let a

scattering material—a small piece of carbon, say—be located at P_1. As explained in the preceding section, the electrons of this scatterer should experience accelerations in the direction P_1z_1 as a result of the passage of the primary beam, and the scatterer should emit a secondary or scattered beam. The intensity of this scattered beam should be a maximum in the plane yOx_1, and should be zero in the direction z_1z_1'. If this analysis be correct, the intensity of the X-rays scattered by a substance at P_1 should vary from zero in a direction P_1z_1 to a maximum in the direction P_1P_2.

Experiments testing this conclusion were performed by Barkla.[1] He found that the intensity of the scattered radiation

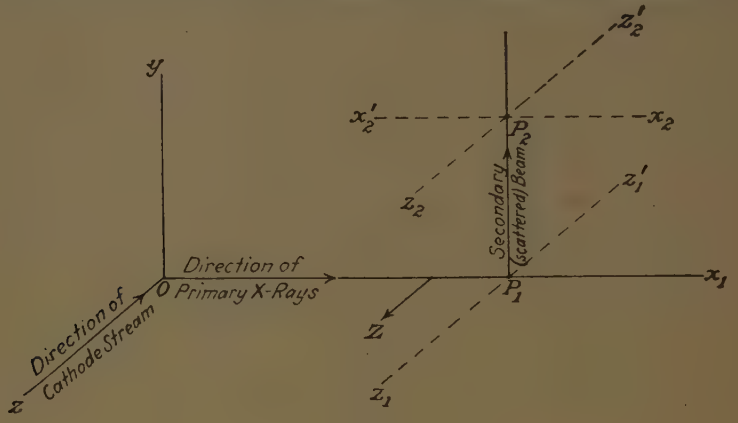


FIG. 124.

in the direction of P_1z_1, while not zero, was considerably less than the intensity in the direction P_1P_2. This indicates that the primary beam is at least *partially* polarized, though not completely polarized. A little further consideration indicates that this is just what we should expect. We assumed, at the beginning of the above discussion, that the electrons of the cathode stream are brought to rest by accelerations directed in the direction Oz. If we attempt to picture the sequence of events by means of which a swiftly moving electron is brought to rest by collision with the atoms of the target at O, we should conclude that rarely will an electron be stopped by a single "head on" collision with an atom. In the general case, an electron will

[1] *Proc. Roy. Soc.* (London), vol. 77, p. 247 (1906).

pursue a zigzag course and will collide with many atoms before being brought to rest. While the preponderance of accelerations may be in the general direction Oz, accelerations in quite different directions are to be expected. In the primary beam, therefore, the Z components of the electric vector should predominate, but Y components are also to be expected. This means that the intensity of the X-rays scattered from P_1 in the direction of P_1P_2 should be greater than in the direction P_1z_1—which is what Barkla observed.

With the *secondary* beam of X-rays proceeding in the direction P_1P_2, however, the situation is different. This secondary beam is produced by the acceleration of electrons at P_1 due to the passage of the primary beam. On account of the transverse nature of electromagnetic radiation, this primary beam, regardless of its state of polarization, can accelerate electrons at P_1 only in directions lying in the plane defined by $P_2P_1z_1$, *i.e.*, in directions at right angles to P_1x_1. Consequently, the electric vector of the *secondary* beam proceeding in the direction P_1P_2 must lie *entirely* in the plane defined by $P_2P_1z_1$; *i.e.*, this secondary beam must be *completely* plane polarized. If, then, this secondary beam be allowed to pass over a second scatterer placed at P_2, the intensity of the *tertiary* radiation sent out from P_2 should vary from *zero* in the direction P_2z_2 to a maximum in the direction P_2x_2. Compton and Hagenow[1] have shown that, after eliminating various errors, the intensity of the tertiary radiation scattered in the direction P_2z_2 is zero within the limit of error of measurement, and, therefore, *as electromagnetic theory predicts*, the secondary beam is *completely* polarized.

The ether-pulse theory was, thus, very successful in explaining many of the observed phenomena of X-rays; indeed, in common with other phases of classical theory, the ether-pulse theory *is still* an important factor. But there was gradually accumulated a mass of data which the ether-pulse theory could not explain. Again, as in other branches of physics, the quantum theory came, more or less successfully, to the rescue. We shall return to this point again after we have discussed the work of Laue, Friedrich and Knipping, Bragg, Moseley, and others, which led to a better understanding of the origin and nature of X-rays.

4. Characteristic Secondary Radiation.—It will not serve our purpose to go into a detailed discussion of the development of

[1] *Jour. Optical Soc. Amer.* and *Rev. Sci. Inst.*, vol. 8, p. 487 (1924).

the subject of X-rays from the introduction of the ether-pulse theory, in the closing years of the nineteenth century, to the discovery by Laue and Friedrich and Knipping, in 1912, of the action of a crystal grating in analyzing a beam of X-rays into its component wave lengths. But no discussion of X-rays, however brief, would be complete without at least reference to the classical work of Barkla,[1] in the decade preceding 1912, which gave a deeper insight into X-ray phenomena and, in large measure, prepared the way for the very remarkable series of advances which began in 1912.

Mention was made, on page 456, of the observation of Winkelmann and Straubel that a beam of X-rays incident onto a piece of Iceland spar was transformed into characteristic "spar" rays the quality of which, as measured by absorption in paper, was quite different from that of the incident beam. Barkla and his collaborators made a thorough and systematic study of this phenomenon of the emission of characteristic *secondary* radiation by a substance when a *primary* beam is incident onto the substance.

We may illustrate the fundamental principles involved by describing a simple but instructive experiment with visible light. Prepare a finely divided suspension of some such material as gum mastic in water.[2] Place the suspension in a rectangular glass box C (Fig. 125) and illuminate it by a beam of white light, as shown. The suspension will appear white when viewed from some such position as point O; that is to say, the suspension *emits*

[1] Among the papers by Barkla and his collaborators may be mentioned the following: BARKLA and SADLER: "Homogeneous Secondary Roentgen Radiation," *Phil. Mag.*, vol. 16, p. 550 (1908); BARKLA and SADLER: "The Absorption of Roentgen Rays," *Nature*, vol. 80, p. 37 (1909); BARKLA: "Phenomena of Roentgen-ray Transmission," *Proc. Cambridge Phil. Soc.*, vol. 15, p. 257 (1909); BARKLA and NICOL: "X-ray Spectra," *Nature*, vol. 84, p. 139 (1910); BARKLA: "Spectra of Fluorescent Roentgen Radiations," *Phil. Mag.*, vol. 22, p. 396 (1911); Barkla: "Absorption of X-rays and Fluorescent X-ray Spectra," *Phil. Mag.*, vol. 23, p. 987 (1912).

The student is urged to read these papers, not only because of their very great historical importance but also because they constitute a background on the basis of which subsequent advances may be better understood and appreciated.

[2] A suitable suspension is readily prepared by dissolving a small quantity of mastic in alcohol and then pouring a few drops of this solution into a beaker of water.

or scatters in the direction of O a radiation of the same quality[1] as is incident onto it. Consequently, a piece of absorbing glass, say blue, will produce the *same* reduction in the apparent brightness of the box as viewed from point O, whether the glass be put in the *primary* beam at A or in the *secondary* beam at B. Conversely, if an absorbing screen is observed to produce the same reduction in the brightness of the box whether the screen be placed at A or at B, we may conclude that the secondary radiation emitted by the material in the box is of the same quality as the primary incident radiation.

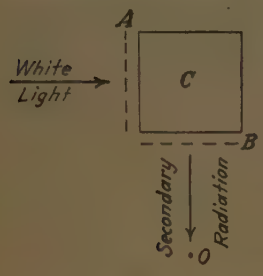


FIG. 125.

Now replace the suspension in the glass box by a solution of some fluorescent material, such as fluoresin. The glass box, when illuminated by white light, will no longer appear white but will emit a fluorescent radiation, blue, green, or red, *characteristic* of the solution.[2] An absorbing screen now will *not* in general absorb the same proportion of the primary beam when placed at A as of the secondary beam when placed at B. Conversely, if we observe that a given absorbing screen does *not* absorb the same fraction of the secondary beam when placed at B as of the primary beam when placed at A, we may conclude that the *quality* of the secondary radiation reemitted by the contents of the box is different from the quality of the *primary* beam. Incidentally, if the glass box contains a mixture of the scattering suspension and the fluorescent solution, the secondary radiation emitted from the box will contain partly scattered, partly fluorescent, light.

Barkla showed that the secondary X-ray radiation emitted by a substance (which we shall refer to as the "secondary emittor") irradiated by a *primary* beam of X-rays is made up partly of *scattered* X-rays, the quality (hardness) of which is (practically) identical with the hardness of the primary beam, and partly of

[1] The particles of the suspension are assumed large enough so that the well-known Tyndall effect plays no role in the scattering process.

[2] The *quality* of this fluorescent radiation is independent of the *quality* of the primary radiation. According to Stokes' law, however, the exciting primary radiation must be of shorter wave length, or must contain components of shorter wave length, than the wave length of the fluorescent radiation. Red light cannot excite blue-green fluorescence.

fluorescent rays, the quality of which is characteristic of the secondary emittor. Barkla's conclusions were based upon a study of the mass absorption coefficient, μ/ρ (see equation (3)) of both the primary and the secondary beam in some standard substance, such as aluminum, as compared with the absorption in other substances. Schematically, let a primary beam of hard X-rays from a target T (Fig. 126), after passing through holes in lead screens S_1S_1, fall upon the secondary emittor E. Let the secondary beam, taken off, say, at right angles to the primary beam, after passing screens S_2S_2, enter the ionization chamber C by means of which the intensity of the secondary beam can be measured either with or without slabs of absorbing material placed at A or at B.

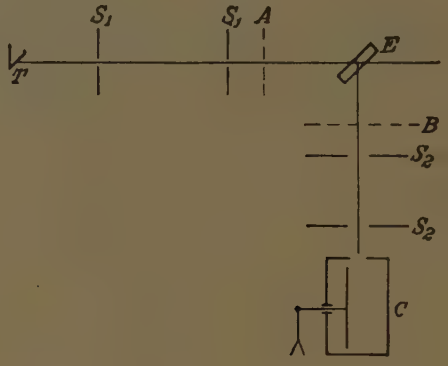


FIG. 126.—Schematic arrangement for studying secondary radiation.

When the secondary emittor is of some light material, such as carbon, an aluminum absorbing screen placed at B absorbs (*nearly*) the same fraction of the secondary beam as it does of the primary beam when placed at A. This shows that the *quality* of the secondary beam as measured by its absorption in aluminum is (nearly) the same as that of the primary beam. The primary beam has been *scattered* by the secondary emittor.

If, however, a heavier material, such as silver, be substituted for the carbon, the absorption coefficient of the secondary beam in aluminum is no longer the same as that of the primary beam. The mass absorption coefficient of the secondary beam is *greater* than that of the primary beam—which indicates that the *quality* (hardness) of the secondary beam is no longer the same as that of the primary. Barkla found that the hardness of the secondary

beam, as measured by its coefficient of absorption in aluminum, is *characteristic* of the material used as secondary emittor. If, for a given (hard) incident primary beam, the mass absorption coefficient in aluminum of the secondary radiation emitted by various substances be plotted as a function of the atomic weight of the emittor, a smooth curve results, as is shown in Fig. 127. The heavier the secondary emittor the more penetrating its secondary radiation This secondary radiation is, thus, seen to be *characteristic* of the emittor. By using various emittors, we can obtain secondary radiations of various qualities as measured by absorption coefficients in aluminum.

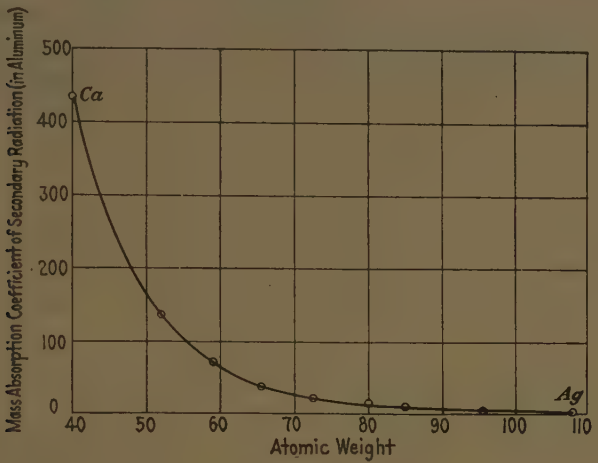


FIG. 127.—The quality of the secondary radiation from various elements as a function of atomic number. The absorption of the radiation by aluminum is taken as an index of quality.

If the absorption coefficients of such a series of secondary radiations obtained from a series of emittors of different atomic weights be measured in some absorber such as iron or copper and these values be compared with the absorption coefficients of these same radiations in aluminum, a curve of the type shown in Fig. 128 results. Point *a* corresponds to a "soft" radiation which has a large coefficient of absorption in aluminum. For more penetrating radiations, the coefficients of absorption in both aluminum and iron decrease along the line *ab*. At *b*, which corresponds to a radiation the absorption coefficient of which in aluminum is about the same as that of the secondary radiation from an iron *emittor*, the absorption coefficient of the radiation in

the iron *absorber* suddenly increases to point *c*. Thereafter, for more penetrating radiations, the absorption in iron decreases again toward point *d*. Radiations in the range *a* to *b* are emitted by elements of *lower* atomic weight than iron; in the range *c* to *d*, by elements of *higher* atomic weight. The position of the discontinuity *bc* depends, in a perfectly regular way, on the atomic weight of the absorber: the higher the atomic weight of the absorber the greater the penetration (in aluminum) of the radiation at which the discontinuity occurs.

These facts pointed unambiguously to the emission by a secondary emittor of a fluorescent radiation characteristic of the emittor, when the emittor is radiated by a primary beam of sufficient hardness. Barkla called this radiation the *K* fluorescent *radiation* of the emittor. For the heavier absorbers, a second discontinuity was observed beyond point *a* of Fig. 128. This indicated that along with the *K* fluorescent radiation was another and a *softer* fluorescent radiation, which Barkla designated by *L*. Barkla recognized that these *K* and *L* radiations constitute *lines* (or groups of lines) in the fluorescent X-ray spectra of the several secondary emittors. In these X-ray spectra, the mass absorption coefficients in aluminum were somewhat analogous to wave lengths in visible light. The discovery of the action of the crystal grating showed that this analogy has a very real origin.

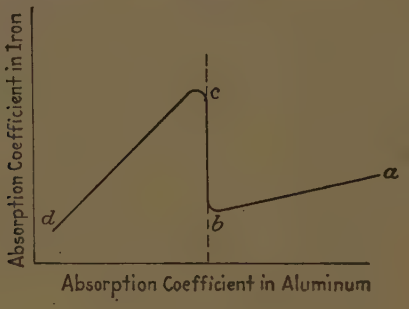


FIG. 128.

5. The Crystal Diffraction Grating. (*a*) *Previous Estimates of X-ray Wave Lengths.*—The researches of Barkla in isolating the *K* and the *L* lines in the fluorescent spectra of the elements pointed unmistakably to something akin to definite wave lengths in X-rays, particularly when the close analogy with the phenomena of scattering and fluorescence in the visible region of the

spectrum was considered. Evidences that X-rays are waves similar to, but shorter than, ordinary light waves were also accumulating from attempts to detect diffraction. We have already referred to the experiments of Haga and Wind (p. 458), who, from the slight evidences of diffraction which they obtained, concluded that X-rays were very short ultra-violet waves, the wave length of which was of the order of 10^{-8} cm. Further attempts to detect diffraction were made by Walter and Pohl,[1] who obtained negative results, from which they concluded that if X-rays were short ultra-violet waves, the wave length could not exceed 10^{-9} cm. Sommerfeld,[2] from a study of the diffraction experiments of Haga and Wind and of Walter and Pohl, concluded that the wave length of X-rays might be of the order of magnitude of 3×10^{-9} cm. And W. Wien,[3] from a measurement of the velocity of the secondary *cathode* rays (*i.e.*, photoelectrons) emitted when X-rays are incident onto a secondary emittor, concluded, by application of Planck's quantum hypothesis, that the wave length of the X-rays must be about 6.7×10^{-9} cm. By 1912, therefore, it was well established, at least as a good working hypothesis, that X-rays are very short electromagnetic waves, the order of magnitude of the wave length being in the neighborhood of 10^{-8} to 10^{-9} cm. There was great need for a *direct* experiment to confirm this hypothesis. This experiment was supplied by Friedrich and Knipping as a result of a brilliant suggestion by Laue,[4] that a crystal, with its regular, three-dimensional array of atoms, should behave toward a beam of X-rays in somewhat the same way as does a ruled diffraction grating toward a beam of light. This experiment very definitely marks the beginning of a new era in the technique of X-ray measurements and in X-ray theory.

(*b*) *Elementary Theory of the Crystal Grating.*[5]—Let us consider a train of plane parallel waves (water, air, or light waves), the crests of which are represented by the straight lines $a, b, c, d \ldots$ (Fig. 129) proceeding in the direction of incidence indicated by the arrow I. Let these waves pass over a series of small obstacles

[1] *Ann. Physik*, vol. 29, p. 331 (1909).

[2] *Ann. Physik*, vol. 38, p. 473 (1912).

[3] *Gesel. Wiss. Göttingen, Nachr.*, vol. 5, p. 598 (1907).

[4] FRIEDRICH, KNIPPING, and LAUE: *Le Radium*, vol. 10, p. 47 (1913); *Ber. Konigl. Bayer, Akad., München*, p. 303 (1912).

[5] See BRAGG, W. L.: *Proc. Cambridge Phil. Soc.*, vol. 17, p. 43 (1912).

1, *2*, *3* . . . arranged in a straight line. These obstacles become secondary sources of disturbance (*i.e.*, they act as scatterers), and a system of secondary circular (or spherical, as the case may be) wavelets surrounds each obstacle, as shown, the circles being drawn to represent correct phase relations among the systems of wavelets. It is observed that these secondary wavelets have, in general, a random distribution with respect to each other, except in the *one* direction indicated by the arrow *R* where there is a tendency for the wavelets to *combine* into a series of envelopes which gives rise to a *reflected* wave train pro-

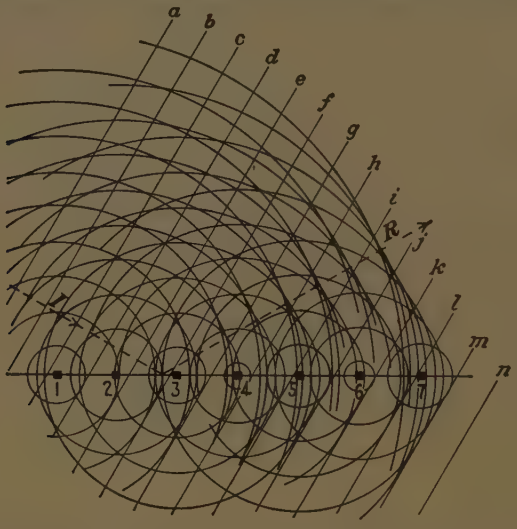


FIG. 129.—Schematic representation of the secondary rays from centers of disturbance *1*, *2*, *3* . . . when set into forced vibrations by the incident primary waves *a*, *b*, *c* . . .

ceeding in the direction *R*. This series of obstacles then causes a small fraction of the incident beam to be, in effect, reflected according to the well-known law of reflection that the angle of incidence equals the angle of reflection.

Next, let us consider the effect on an incident beam of a three-dimensional array of such "diffracting centers," arranged in regular rows, columns, and layers. Figure 130 shows three rows *AA*, *BB*, *CC* of such centers, in one plane only of course, the distance between the rows being *d*. (We imagine the array to be extended in three dimensions.) Let an incident beam of wave length λ be incident onto this array at a "glancing angle" θ of 30 degrees. As shown in Fig. 129, each of these rows of

diffracting centers will give rise to a reflected beam, and we shall have the reflected beams $O_1 1$, $O_2 2$, $O_3 3$, etc. As drawn in the figure, the phase relations among these reflected beams are such that the crests of the waves in the train $O_3 3$ exactly coincide with the troughs of the train $O_1 1$. These two beams will, therefore,

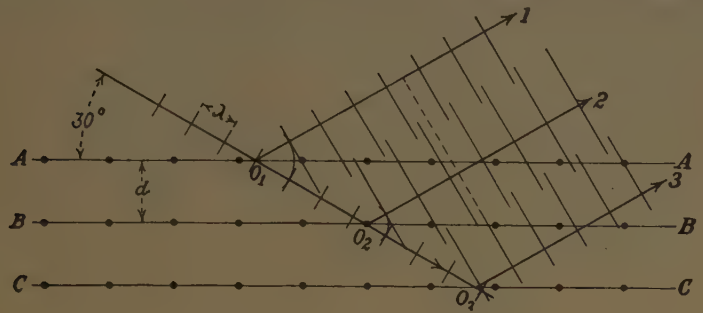


FIG. 130.—The destructive interference of secondary wave trains.

destructively interfere and will cancel each other. In like manner, $O_2 2$ will interfere with $O_4 4$; and so on, for all other pairs of reflected waves. The net result is that there is *no* wave train reflected from the three-dimensional array of diffracting centers. *In general*, for any combination of λ, d, and θ, it will be possible to

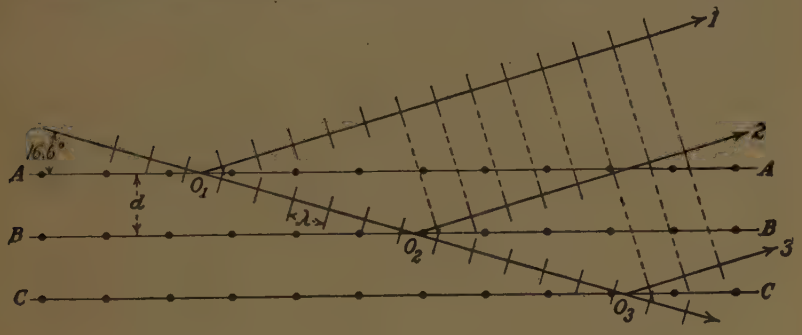


FIG. 131.—The reinforcement of secondary wave trains.

find *pairs* of reflected beams, which, in like manner, will destructively interfere with each other, and no reflected beam will result.

It is possible, however, to choose *particular* sets of values of λ and θ for a given d such that the reflected waves are all in phase, as is shown in Fig. 131, where, for the particular values of

λ and d, for which the construction was made, the glancing angle θ is 16.6 degrees. The crests of the trains $O_1 1, O_2 2, O_3 3$ . . . are seen to coincide; the reflected wave trains reinforce each other; and a reflected *beam* results. The condition that these individual reflected trains shall be in phase is, obviously, that the reflected train $O_2 2$ shall be exactly 1 wave length, or an integer multiple of wave lengths, behind the train $O_1 1$. The simple relation among λ, d and θ to which this requirement leads is at once seen from Fig. 132, which shows the incident beam I reflected at O_1 and O_2, as in Fig. 131. The line ab is perpendicular to the reflected rays $O_1 1$ and $O_2 2$. The length of path $O_1 O_2 b$ is greater than the length of the path $O_1 a$ by the length of the broken line $cO_2 b$, the line Oc being perpendicular to $O_1 O_2$. The length of the

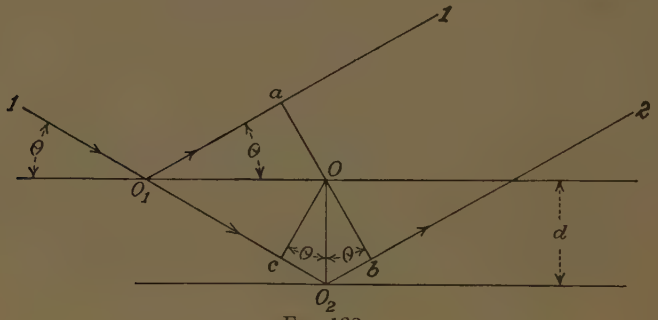


FIG. 132.

broken line $cO_2 b$ is, obviously, $2d \sin \theta$. The condition that there should be a reflected beam is, therefore, that

$$n\lambda = 2d \sin \theta \qquad (20)$$

where n is an integer. This is known as *Bragg's law*.

Figure 133 represents one horizontal plane of a three-dimensional array of diffraction centers. There are numerous possible combinations of parallel layers (the planes of which are perpendicular to the plane of the paper) *1*, *2*, *3*, *4* . . . with different distances d_1, d_2, d_3 . . . between planes. Now, imagine a parallel wave train, containing a *continuous spectrum* of wave lengths, to be incident onto this group of diffracting centers as shown by the parallel arrows a, b, c, d . . . If, in this incident heterochromatic wave train, there is a wave length λ_2 such that

$$n\lambda_2 = 2d_2 \sin \theta_2$$

where n is an integer, d_2 is the distance between the set of planes numbered "2," and θ_2 is the glancing angle of incidence between the direction of the incident radiation and the planes, there will be reflected from this group of planes a beam A, of wave length λ_2, which will proceed in the direction of the arrow A. Similarly, we may have reflected beams B, C, D . . . in different directions. In order that a beam shall be reflected through a measur-

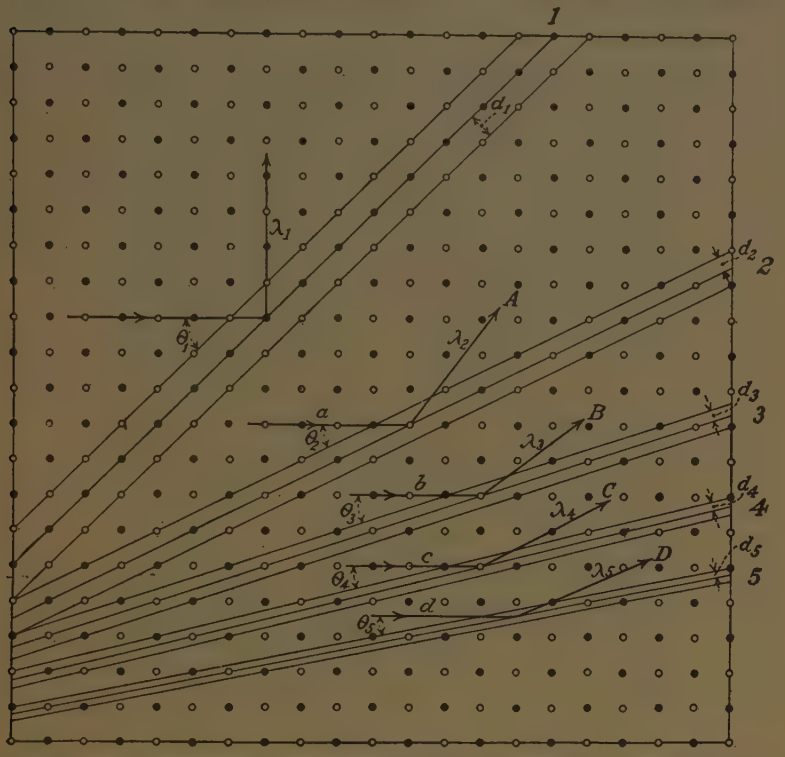


FIG. 133.—Schematic representation of the reflection of monochromatic wave trains of X-rays by a crystal of NaCl when radiated by a heterochromatic incident beam.

able angle, however, it is necessary that d shall be not too great compared to λ.

Now, (1) *if* a beam of X-rays is comprised of waves the wave length of which is of the order of magnitude of 10^{-8} or 10^{-9} cm., and (2) *if* a crystal is composed of a regular array of atoms which, it might be expected, act as diffraction centers for X-rays, then, on passing a beam of X-rays through a crystal somewhat

after the manner of the diagrammatic arrangement of Fig. 133, beams of X-rays corresponding to A, B, C . . . should be reflected in various directions from the crystal. It was this experiment, suggested by Laue, that Friedrich and Knipping tried.

6. The Experiment of Friedrich, Knipping, and Laue.—By means of suitable screens S_1S_2 (Fig. 134), a narrow pencil of X-rays from the target T was allowed to pass through a crystal C beyond which was a photographic plate PP. After an exposure of many hours, it was found on developing the plate that, in addition to the interior central image at O, where the direct beam struck the plate, there were present on the plate many regularly arranged, but fainter, spots, indicating that the incident X-ray beam had been reflected from the various crystal planes, exactly in accordance with the discussion of the preceding

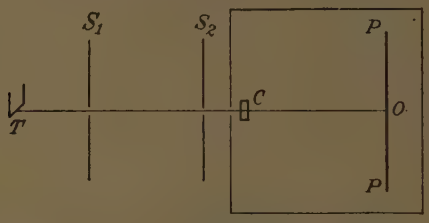


FIG. 134.—The arrangement by which Friedrich and Knipping discovered the action of a crystal on a beam of X-rays.

section. Figure 135 shows such a photograph, taken by Dr. George L. Clark,[1] of an iron crystal. The perfect symmetry of the spots about the central image is clearly brought out. In their original paper,[2] Friedrich, Knipping, and Laue, from an analysis of a series of photographs of a crystal of zinc blend oriented at various angles with respect to the incident pencil, concluded that there were present in the X-ray beam wave lengths varying between $1.27 \cdot$ and $4.83 \cdot 10^{-9}$ cm.—values in excellent agreement with previous estimates. This positive result at once proved the correctness of the *two* postulates underlying the experiment: (1) that X-rays are electromagnetic waves of definite wave lengths and (2) that the atoms of a crystal are

[1] The author is indebted to Dr. Clark and to the McGraw-Hill Book Company, Inc., for permission to use this photograph.

[2] Loc. cit. p. 473.

arranged in a regular three-dimensional lattice, as may be inferred from the external symmetry of crystals.

As a result of this famous experiment of Friedrich, Knipping, and Laue, two new and very important fields of investigation were at once opened up: (1) the study of X-ray spectra and the determination of wave lengths and (2) the study of crystals with particular reference to the arrangement of atoms in crystals. These fields are, to a certain extent, mutually interdependent,

FIG. 135.—Laue photograph of an iron crystal (*taken by Dr. George L. Clark*).

since the crystal grating is such an indispensable part of any X-ray spectrometer. In the following sections, we shall discuss some of the more important aspects of X-ray spectra and their interpretation. For more detailed presentations of X-ray phenomena and their applications in chemistry, crystallography, biology, medicine, and industry, we refer the student to the numerous standard treatises.[1]

[1] COMPTON, A. H.: "X-rays and Electrons" (1926); DE BROGLIE, M.: "X-rays" (translated by Clark) (1924); SIEGBAHN, M.: "The Spectroscopy of X-rays" (translated by Lindsay) (1925); CLARK, GEORGE L.: "Applied X-rays" (1927).

7. The X-ray Spectrometer.—Immediately following the announcement by Friedrich, Knipping, and Laue of their successful experiment, many investigators took up a study of the new phenomenon. Among these were W. H. and W. L. Bragg,[1] to whom we are chiefly indebted for the early development of the X-ray spectrometer.

A spectrometer of the Bragg type is shown diagrammatically in Fig. 136 (*a*). X-rays from the target T of an X-ray tube pass through two narrow slits S_1 and S_2, a few hundredths or tenths of a millimeter wide, the edges of which are made of some

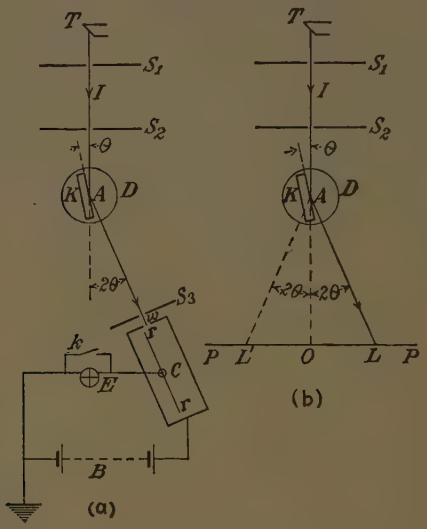


FIG. 136.—(*a*) The X-ray spectrometer, ionization method; (*b*) the X-ray spectrometer, photographic method.

material, such as lead or gold, which is very opaque to X-rays. This ribbon-shaped incident beam of X-rays I falls at a glancing angle θ onto the cleavage face of a crystal K—rock salt, calcite, mica, gypsum, quartz, etc.—which is mounted on a table D the angular position of which can be accurately read by verniers or micrometer microscopes. The reflected beam of X-rays, which makes an angle 2θ with the incident beam, enters, through the "window" w, an ionization chamber C, by means of which

[1] BRAGG, W. L.: "Specular Reflection of X-rays," *Nature*, vol. 90, p. 410 (December, 1912); BRAGG, W. H., and BRAGG, W. L.: "Reflection of X-rays by Crystals," *Proc. Roy. Soc.*, London vol. 88, p. 428 (July, 1913); BRAGG, W. H.: "X-rays and Crystals," *Nature*, vol. 91, p. 477 (July, 1913).

(see Fig. 115) the intensity of the reflected beam may be measured. By suitably turning the table D about the axis A, the incident beam may be made to strike the face of the crystal at any glancing angle θ. The ionization chamber C is mounted on an arm (not shown) by means of which the chamber can be rotated about the axis A so as to admit the reflected beam through the window W. For protection against stray, scattered radiation, a third slit S_3 is attached to the chamber.

For photographic registration, the ionization chamber may be replaced by a photographic plate PP (Fig. 136(b)). With the crystal set at a glancing angle θ, the reflected beam will strike the plate at L (or at L', if the crystal be "reversed"). From the position O at which the direct beam strikes the plate, the distances OL and OA and, hence, the angles 2θ and θ may be determined. The wave length λ is then obtained from the formula

$$n\lambda = 2d \sin \theta$$

The distance d between the reflecting planes of a crystal such as NaCl is determined as follows: From his investigations, Bragg showed[1] that, in the rock-salt crystal, the Na and the Cl atoms (more accurately, the Na and the Cl *ions*. See Chap. XI, Sec. 2) occupy alternate positions at the corners of elementary cubes in the cubic lattice characteristic of the crystal, the arrangement being similar to that shown in Fig. 133, which represents one plane of atoms. Taking the atomic weight of chlorine as 35.46 and of sodium as 23.00, the molecular weight of NaCl is 58.46. Therefore, 58.46 grams of the NaCl contain $2N_0$ atoms, *i.e.*, N_0 atoms of Na and N_0 atoms of Cl, where $N_0 = 6.06 \times 10^{23}$ is Avogadro's number. The number of atoms n in 1 *cm.-cube* of rock salt is

$$n = \frac{2 \times 6.061 \cdot 10^{23}}{58.46} \times \rho \qquad (21)$$

where $\rho = 2.163$ is the density of NaCl. If d is the distance between the center of one atom and the next along the edge of the cube, $1/d$ is the number of atoms in a row of atoms 1 cm. long, and the number of atoms in the centimeter-cube is

$$n = \frac{1}{d^3} \qquad (22)$$

[1] See BRAGG: "X-Rays and Crystal Structure."

Equating equations (21) and (22) and solving for d, which is the desired distance between the (cleavage) planes in NaCl, we find

$$d = 2.81 \times 10^{-8} \text{ cm.}$$

The value of d is seen to be dependent on M, the molecular weight of rock salt; on ρ, the density of rock salt; and on Avogadro's number N_0. The values of N_0 and ρ are not known to much better than 0.1 per cent. There is, hence, a corresponding uncertainty in the value of d. At present, measurements of X-ray wave lengths can be made with a precision many fold greater than the best measurements of M, N_0, or ρ. It is, therefore, customary to assign an arbitrary value, the best obtainable by experiment, to the grating space of some crystals, as, for example, the value of 2.81400×10^{-8} cm. for NaCl, and to express X-ray wave lengths in terms of this value. The grating space of other crystals are then compared to this arbitrary value for NaCl as a standard.[1]

Table I gives some of the crystals used in X-ray spectroscopy and the corresponding grating spaces.

TABLE I.—SOME CRYSTALS USED IN X-RAY SPECTROSCOPY

Crystal	Grating space, centimeters times 10^8
Rocksalt, NaCl	2.814
Calcite, $CaCO_3$ (18°C.[1])	3.02904
Quartz, S_1O_2	4.247
Gypsum, $CaSO_4 \cdot 2H_2O$	7.578
Potassium ferrocyanide, $K_4Fe(CN)_6$	8.408
Mica	9.93
Sugar	10.57
Palmitic acid	35.59
Stearic acid	38.7

[1] Of course, the grating space of any crystal depends upon its temperature. The grating space of calcite increases 0.00003×10^{-8} cm. per degree (centigrade) increase of temperature in the neighborhood of 20°C. For NaCl, the corresponding change is approximately 0.00011×10^{-8} cm. per degree.

There are numerous alternative arrangements for using a crystal in connection with an X-ray spectrometer. Among these may be mentioned that of Seemann,[2] in which the two collimating slits S_1 and S_2, of Fig. 136, are omitted and in their place

[1] The International Critical Tables give 3.028×10^{-8} cm. as the grating space of calcite.

[2] *Ann. Physik*, vol. 49, p. 470 (1916)

is used a wedge W (Fig. 137) the edge of which is placed close to and parallel to the cleavage face of the crystal. For more penetrating radiation, Siegbahn[1] has used the arrangement shown in Fig. 138, in which the incident beam passes *through* the crystal and is reflected from the inner planes. The second slit S_2 is placed immediately behind the crystal and is rigidly connected to the table D on which the crystal is mounted. The table can be rotated about an axis passing through S_2.

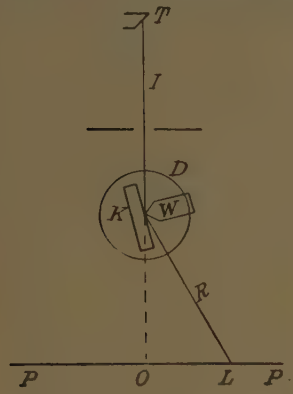


FIG. 137.—The Seemann "slit."

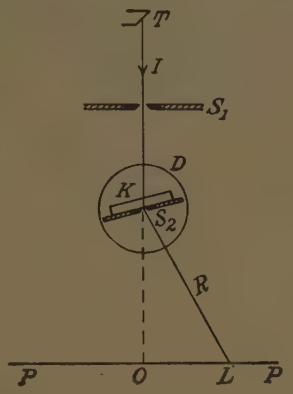


FIG. 138.—A slit system employed by Siegbahn.

8. Bragg's Discovery of Monochromatic Characteristic Radiations.—With a beam of X-rays incident onto the cleavage face of a (mica) crystal, as shown in Fig. 136(*b*), W. H. Bragg found[2] that there was produced on the photographic plate PP an image or line at L in the exact position to be expected if the beam were reflected from the crystal in accordance with the theory outlined in Sec. 5. He then replaced the photographic plate by an ionization chamber and found that when the chamber was so placed that the reflected beam entered the chamber, an ionization current was produced, which current he took as a measure of the intensity of the reflected beam. Then, using a rock-salt crystal and an X-ray tube with a platinum target, he investigated the intensity of the reflected beam for various glancing angles θ. He found that the intensity did not vary uniformly with angle but that at certain angles the intensity rose to a sharp maximum. When intensity was plotted as a function of angle, a curve

[1] "The Spectroscopy of X-rays" (English translation), p. 57.

[2] *Nature* (Jan. 23, 1913).

similar to that shown in Fig. 139 was obtained. A group of three maxima, a_1, b_1, and c_1, was observed at the respective angles θ of 9.9, 11.6, and 13.6 degrees. A second group of three maxima, a_2, b_2, and c_2, was observed at approximately double these angles. This second group is similar, as regards relative intensities of the maxima, to the first group. Bragg interpreted the maxima a_1, b_1 and c_1 as three monochromatic lines; and the second group of maxima a_2, b_2, and c_2 as second-order reflections

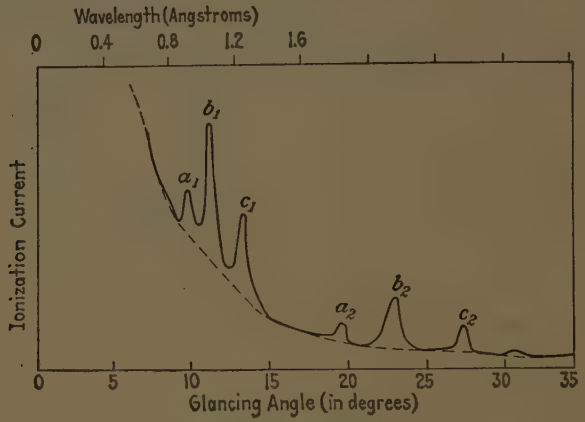


FIG. 139.—Bragg's curve for the energy distribution in an X-ray spectrum, showing the characteristic lines *a*, *b*, *c*.

of the lines a_1, b_1, and c_1. He computed their wave lengths by the formula

$$n\lambda = 2d \sin \theta$$

where $n = 1$ for the "lines" a_1, b_1, and c_1; and $n = 2$ for the second-order lines a_2, b_2, and c_2. A third-order peak b_3 was observed at 36.6 degrees. Using the present accepted value of $d = 2.814$ Ångströms for rock salt, the wave lengths corresponding to these three lines were as follows (Table II):

TABLE II.—FIRST MEASUREMENTS OF X-RAY WAVE LENGTHS BY BRAGG (PLATINUM TARGET)

Line	θ, degrees	Sin θ	n	λ, Ångströms
a_1	9.9	0.172	1	0.97
b_1	11.6	0.200	1	1.13
b_2	23.6	0.400	2	1.13
b_3	36.6	0.597	3	1.12
c_1	13.6	0.235	1	1.32

Curves similar to Fig. 139 were obtained with other crystals—calcite, iron pyrites, zinc blend, etc.—the only difference being that the maxima occurred at different glancing angles, indicating that each crystal had a characteristic grating space d. Bragg convinced himself, however, that these respective maxima for different crystals always represented the same monochromatic radiation, since, for example, the absorption in aluminum of peak b_1 was always the same, whatever the crystal used. In short, the interpretation of the curve in Fig. 139 became clear: the peaks are *spectral lines* the wave lengths of which, as Bragg showed later,[1] are *characteristic of the target emitting the rays*. These monochromatic lines are superimposed on a *continuous* spectrum[2] represented by the partially dotted line in Fig. 139. Curves of the type shown in Fig. 139, therefore, represent (subject to certain corrections to be mentioned later) the distribution of *energy* in the X-ray spectrum, continuous and characteristic combined, of an element.

9. Moseley's Law.—In two classic papers,[3] Moseley presented a systematic study of the characteristic radiations emitted by various targets, using a photographic method similar in principle to that shown in Fig. 136(b). He found a larger number of characteristic lines than did Bragg and, also, that these lines could, in general, be classified into two groups: (1) a group of shorter wave lengths, which, by means of the value of absorption coefficients in aluminum, he identified with Barkla's K characteristic secondary radiations and (2) a group of lines of longer wave length, similarly identified with Barkla's L radiation. Unlike the optical spectra, the X-ray characteristic spectra of the elements were found to be similar from element to element, homologous lines occurring, in general, at shorter wave lengths the greater the atomic weight of the element in which the lines originate.

Table III, taken from Moseley's paper, shows the wave lengths found by him for the two strongest lines of the K series, which lines Moseley named $K\alpha$ and $K\beta$. In searching for a relation between the frequency of a given line, say, the $K\alpha$ line, and some property of the atom in which the line originated, Moseley first

[1] *Proc. Roy. Soc.*, London, vol. 89, pp. 246, 430 (1913).

[2] See also MOSELEY and DARWIN: *Phil. Mag.*, vol. 26, p. 210 (1913).

[3] *Phil. Mag.*, vol. 26, p. 1024 (1913) and vol. 27, p. 703 (1914). The student should consult the original papers.

observed that the frequency did not vary regularly with the atomic weight, as is shown by curve A (Fig. 140) in which the square root of the frequency is plotted against the atomic weight.

TABLE III.—MOSELEY'S VALUES FOR THE WAVE LENGTHS OF (HIS) α AND β LINES OF THE K SERIES

Element	Wave length, Ångströms		Atomic weight	Atomic number
	α	β		
Al	8.364	7.912	26.96	13
Si	7.142	6.729	28.06	14
Cl	4.750	.....	35.46	17
K	3.759	3.463	39.09	19
Ca	3.368	3.094	40.07	20
Ti	2.758	2.524	47.9	22
Va	2.519	2.297	50.96	23
Cr	2.301	2.093	52.01	24
Mn	2.111	1.818	54.93	25
Fe	1.946	1.765	55.84	26
Co	1.798	1.629	58.97	27
Ni	1.662	1.506	58.69	28
Cu	1.549	1.402	63.57	29
Zn	1.445	1.306	65.38	30
Y	0.838	.....	89.0	39
Zr	0.794	.....	91	40
Nb	0.750	.....	93.1	41
Mo	0.721	.....	96.0	42
Ru	0.638	.....	101.7	44
Pd	0.584	.....	106.7	46
Ag	0.560	.....	107.88	47

Bohr had recently proposed his theory of the origin of spectra, in which theory the charge Z on the nucleus played a fundamental role. According to Bohr's theory, the frequency ν of a spectral line is given by (see equation (33), Chap. X)

$$\nu = Z^2 \cdot \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

from which

$$\sqrt{\nu} \propto Z.$$

Rutherford had shown, from his experiments on the scattering of α particles, that the value of the nuclear charge, for a given atom, is very approximately one-half the atomic weight; and

Barkla had shown, from experiments on the scattering of X-rays, that the number of electrons surrounding the nucleus is, also, approximately one-half the atomic weight. So, silicon, for example, atomic weight 28.06, should have 14 extranuclear electrons. It is the fourteenth element in the periodic system. The ordinal number of an element should, therefore, be identical with Z, the charge (taking $e = 1$) on the nucleus. Moseley, accordingly, assigned atomic numbers Z (column five of Table III) to the elements which he had investigated, and, in accord-

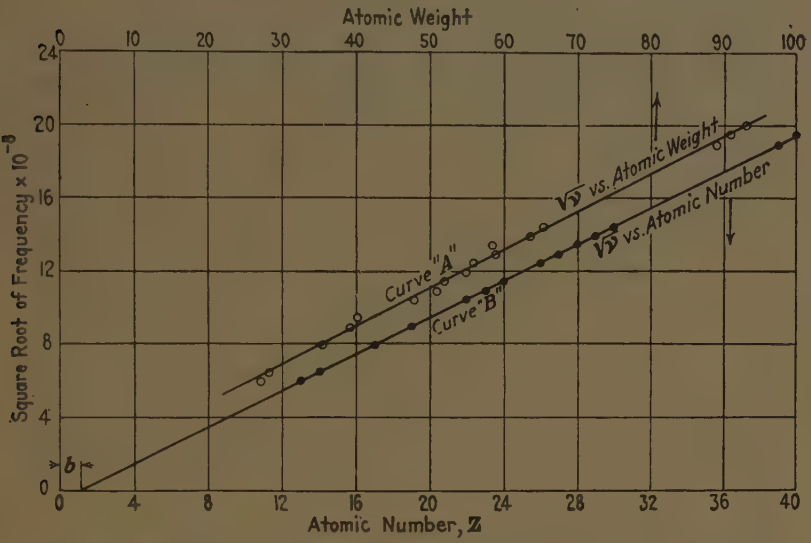


FIG. 140.—Moseley's curve showing the relation between the frequencies of X-ray lines and atomic number.

ance with the relation suggested by Bohr's equation, he plotted a curve between $\sqrt{\nu}$ and the atomic number Z. Such a plot of Moseley's data for the $K\alpha$ line is shown in Fig. 140, curve B. The graph is seen to be a straight line, with a small intercept $b = 1$ on the Z-axis. It is obvious from a comparison of the two curves A and B, of Fig. 140, that, so far as concerns the determination of the *frequency of characteristic lines*, *atomic number* is a much more fundamental quantity than atomic weight.

Empirically, the relation between the frequency ν of the $K\alpha$ line and Z, as determined from Fig. 140, curve B, is

$$\nu = 0.248 \times 10^{16}(Z - 1)^2 \qquad (23)$$

In Bohr's equation (33), Chap. X, for the frequency ν of a spectral line, if we set $\tau_1 = 1$ and $\tau_2 = 2$, we obtain for ν

$$\nu = 0.328 \times 10^{16} \cdot Z^2 (1/1^2 - 1/2^2) \qquad (24)$$

$$= 0.246 \times 10^{16} \cdot Z^2 \qquad (24')$$

by inserting the numerical values of m, e, and h. Except for the slight correction to Z, equations (23) and (24′) *are seen to be almost identical.* We may, therefore, conclude that equation (24), in which Z is to be replaced by $(Z - 1)$, gives to a first approximation the frequency of the $K\alpha$ line of the elements.

This leads to a very far-reaching conclusion as to the origin of the $K\alpha$ line: From Bohr's interpretation of the meaning of $\tau_1 = 1$ and $\tau_2 = 2$ in equation (33), Chap. X, we conclude that *the $K\alpha$ line originates when an electron transfers (or jumps) from an orbit corresponding to $\tau = 2$ to an orbit corresponding to $\tau = 1$.* We can thus form a reasonably concrete picture of the atomic processes (in terms of Bohr's theory) which lead to the production of the $K\alpha$ line in the X-ray spectrum of an element. In a normal atom for which $Z \gtrsim 10$, we have seen that there are 2, *and only* 2, electrons in orbits corresponding to quantum number 1; there are 8 electrons, *and only* 8, in orbits corresponding to quantum number 2. The effect of the bombardment of the atoms in the target of the X-ray tube by the swiftly moving electrons of the cathode stream is, if these electrons possess sufficient energy, to "knock" from (some of) the atoms in the target electrons which normally occupy orbits of quantum number 1. To fill the orbits thus made vacant, electrons "drop" from orbits of quantum number 2 to the vacant orbits of quantum number 1 and thereby emit monochromatic radiation—the $K\alpha$ line. In a similar way, the $K\beta$ line may be shown to originate when electrons drop from orbits of quantum number 3 into vacant orbits of quantum number 1. Because of the part which they thus play in the production of the K lines, these 2 electrons, normally occupying orbits for which $\tau = 1$, are called K electrons; and the orbits are called K orbits. Similarly, the electrons normally occupying orbits for which $\tau = 2$ are called L electrons, and the corresponding orbits are L orbits.

This picture affords, also, an explanation, at least qualitative, of the appearance of the factor $(Z - 1)$ instead of Z in equation (23). When, as a result of bombardment by the cathode stream, one of the K electrons is removed from an atom, there is 1 K

electron left near the nucleus. This electron "screens" the nucleus and makes its *effective* nuclear charge 1 unit less; hence, the factor $(Z - 1)$.

Following Moseley's work, the technique of X-ray spectroscopy developed rapidly. New lines were discovered and classified, and their origin in terms of electron transfers were systematically worked out. We shall postpone further discussion of characteristic X-ray spectra until after we have considered the continuous spectrum and related phenomena.

10. The Continuous X-ray Spectrum. (*a*) *Limiting Minimum Wave Lengths and the Determination of h.*—As has been pointed out above, the X-ray spectrum, in general, consists of a characteristic, or line, spectrum superimposed on a continuous spectrum. The positions, *i.e.*, wave lengths, of the *lines* are determined *solely* by the material of the target; their *intensity* is determined, for a given target material and tube current, by the voltage applied to the tube. On the contrary, the *wave-length* characteristics of the *continuous spectrum* are quite independent of the *material* of the target but are determined by the voltage applied to the tube. The *intensity* of the continuous spectrum, for a given tube current, is dependent both on the target material and on the applied voltage as well as on the thickness of the target. In this section, we shall give a brief survey of some of the more important facts concerning the continuous spectrum.

If, with the ionization spectrometer shown diagrammatically in Fig. 136(*a*), the crystal be set at a series of angles θ and the ionization current at each angle be measured, then a curve, plotted between these several ionization currents as ordinates and the values of the corresponding wave lengths determined from the formula $n\lambda = 2d \sin \theta$, as abscissæ, is called *a spectral energy-distribution curve.* A part of such a curve was shown in Fig. 139. A series of four such curves for the radiation from a tungsten target and for applied voltages of 20,000, 30,000, 40,000, and 50,000 volts, respectively, is shown in Fig. 141.[1] Starting at the long-wave-length side, the curves rise to a maximum and then drop rapidly toward zero, the position of the maximum depending on the applied voltage. The curves are seen to be somewhat similar to the black-body curves of Fig. 54, voltage in X-ray radiation playing a role in a rough way

[1] These curves are from the measurements of ULREY, *Phys. Rev.*, vol. 11, p. 401 (1918). They are subject to certain corrections to be mentioned later.

analogous to temperature in black-body radiation. But there is this very important difference between the black-body and the X-ray curves: Whereas the black-body curves, on the short-wave-length side, approach the wave-length axis asymptotically, the X-ray curves meet that axis at finite angles, as is shown at the intersections *a*, *b*, *c*, and *d*, respectively, of Fig. 141. These intersections can be very accurately measured by making readings nearer the axis[1] than the readings shown in Fig. 141. It is seen that the intersections come at shorter wave lengths the higher the voltage. In Table IV are shown the limiting wave lengths—the intersections *a*, *b*, *c*, and *d*, of Fig. 141—and the

TABLE IV.—LIMITING WAVE LENGTHS AND FREQUENCIES IN THE CONTINUOUS X-RAY SPECTRUM AT VARIOUS VOLTAGES

(From Ulrey's data, Fig. 141)

Potential, kilovolts	Limiting wave length, Ångströms	Limiting frequency, times 10^{-18} cm.$^{-1}$
20	0.615	4.87
30	0.405	7.40
40	0.310	9.76
50	0.250	12.0

corresponding limiting (or *maximum*) frequencies for the four voltages. A very simple relation exists between these limiting frequencies and the applied voltage. This relation is shown graphically in Fig. 142, in which the limiting frequency is plotted as ordinates against the applied voltage as abscissæ. The graph is a straight line passing through the origin; the limiting frequency is strictly proportional to the applied voltage, the empirical equation of the curve being

$$\nu_m = 2.43 \times 10^{14} V' \qquad (25)$$

where ν_m is the *maximum* frequency which an applied voltage V' (in *volts*) can generate.

The explanation of this sharp "cutoff," at a limiting minimum wave length, shown by the curves in Fig. 141, and of the simple relation contained in equation (25) illustrates, in a very striking manner, the inadequacy of the classical theory. According to the ether-pulse, *i.e.*, the classical, theory[2] of the production of

[1] See DUANE and HUNT: *Phys. Rev.*, vol. 6, p. 166 (1915).

[2] See Sec. 3, this chapter.

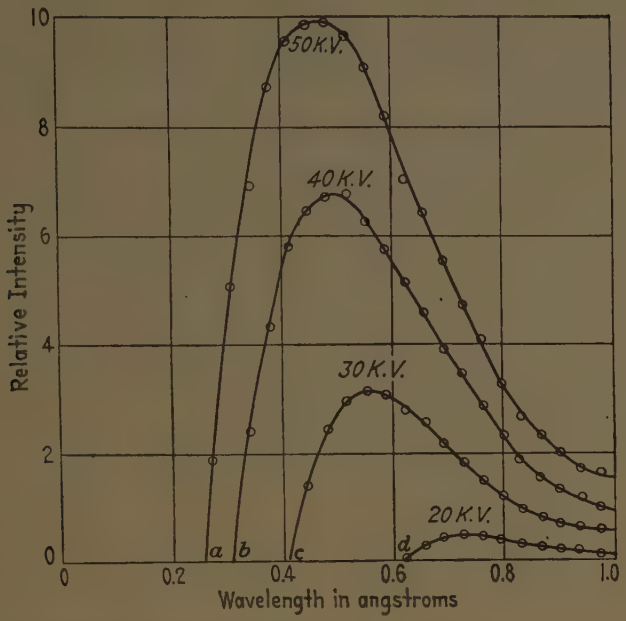


FIG. 141.—Ulrey's curves for the distribution of energy in the continuous X-ray spectrum of tungsten at various voltages.

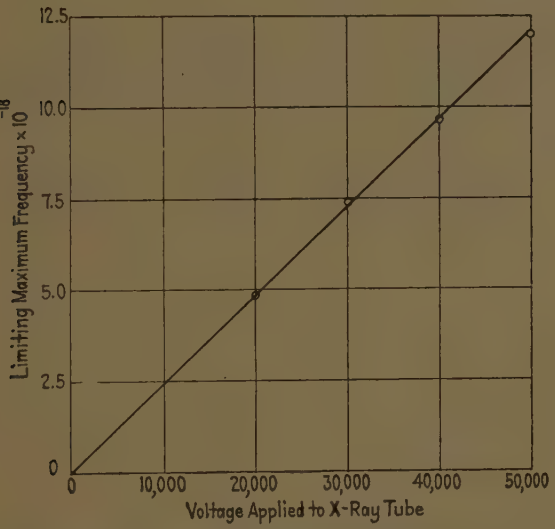


FIG. 142.—The relation between the maximum or limiting frequency and applied voltage.

X-rays, the Fourier analysis of the ether pulses into wave trains should result in an *asymptotic* approach of the X-ray energy-distribution curves to the wave-length axis on the short-wave-length side; whereas experiment requires a *sharp* cutoff. There have been various attempts to postulate a type of ether pulse which should yield such a sharp cutoff, or a limiting maximum frequency, for a given applied voltage. These attempts have been, in general, unsuccessful. In short, the classical theory offers no explanation for this phenomenon.

Again, the quantum theory is more successful. From the standpoint of the sequence of processes involved, the production of X-rays by the bombardment of a target with electrons is the converse of the photoelectric effect. In the latter, monochromatic radiation of frequency ν falling upon a photoelectrically sensitive substance causes the emission of electrons the (kinetic) energies of which, as they leave the suface of the emittor, vary all the way from a *maximum* E_m, given by

$$E_m = \tfrac{1}{2}mv_{\max}^2 = h\nu - \omega_0$$

down to zero. In the production of X-rays, a stream of electrons, all possessing the same kinetic energy E, determined by the potential V applied to the X-ray tube and given by

$$E = Ve$$

where e is the charge of the electron, are incident onto the target of the X-ray tube and cause the emission of *radiation* (X-rays) the frequencies of which vary all the way from a *maximum* frequency ν_m down to zero. Because of the similarity of these two phenomena, it may be expected that Einstein's photoelectric equation (equation (33), Chap. VI)

$$Ve = h\nu - \omega_0$$

which was successful in "explaining" the photoelectric effect should, when "inverted," apply, also, to the phenomenon of X-ray production. In equation (33), Chap. VI, ω_0 was identified with the work required for the photoelectron to escape from the surface of the emittor. Since this work was, at most, equivalent to only a volt or so, it is obvious that in applying equation (33), Chap. VI, to X-ray phenomena we may neglect ω_0 with respect to the other two terms of the equation, since in the pro-

duction of X-rays we are dealing with many thousands of volts and, therefore, $Ve >> \omega_0$. We may, therefore, write, as the equation which expresses the *converse* of the photoelectric process,

$$h\nu_m = Ve \tag{26}$$

where Ve is the energy which is acquired by the electrons in the X-ray tube in "falling" from the cathode of the tube through the potential difference V to the target, and ν_m is the *maximum* frequency of the X-rays produced when these electrons are brought to rest by impact with the atoms of the target. In other words, when an electron possessing kinetic energy Ve collides with, and is brought to rest by, an atom, a *quantum* of (X-ray) energy $h\nu_m$ is emitted, and so long as the kinetic energy of the incident electrons does not exceed Ve, no frequencies greater than ν_m can be emitted. We should, however, expect in addition to ν_m a whole spectrum of *lower* frequencies in the emitted X-ray beam, since, as was pointed out above, in only a very small proportion of cases would it happen that an electron incident upon the target would be brought to rest by a single encounter; and it is only these single encounters which give rise to the frequency ν_m. In the vast majority of cases, an electron would experience many collisions before being brought to rest. At each of these collisions, some of the energy Ve is dissipated. Occasionally, an electron may convert a part or all of its reduced energy into a quantum of frequency less than ν_m. If the target be sufficiently thin—say of very thin gold foil—only a few of the electrons of the incident cathode stream will collide with the atoms of the target, the majority of the electrons passing through the target substantially undeviated. (This phenomenon is utilized in the well known cathode-ray tube developed by Dr. W. D. Coolidge.) It is obvious (1) that only those electrons which collide with atoms can produce X-rays; and (2) that, because of the thinness of the target, the chances that a given electron will dissipate some of its energy before a collision are much less than when thick targets are used. Accordingly, we should expect that a greater proportion of the energy in the continuous spectrum from thin targets should be nearer the ν_m limit, than from thick targets. This is in agreement with experiment.

We thus have a qualitative explanation, on the basis of the quantum theory, of some of the pertinent features of the energy-

distribution curves shown in Fig. 141. The *maximum* frequencies ν_m, corresponding to the points a, b, c, . . . for the respective voltages are emitted as a result of a few of the electrons in the cathode stream, being brought to rest by a single collision with an atom of the target, the relation between ν_m and V being given by

$$h\nu_m = Ve \tag{26}$$

Frequencies lower than ν_m in the X-ray spectrum at a given voltage are emitted as a result of collisions in which only a part of the initial energy Ve of the electron is converted into radiation. In the sum total of collisions between the electrons and the atoms of the target, it might be expected that there would be a "*most probable*" type of collision which would correspond to the peak or maximum of the energy-distribution curve.

With the *shape* of the energy-distribution curve we are not, for the moment, concerned. Rather, let us return to the empirical equation (25) and to the curve (Fig. 142) which showed, in complete agreement with the equation (26), that $V \propto \nu_m$. Writing equation (26) in the form

$$\nu_m = \frac{e}{h}V = \frac{e}{h}\frac{V'}{300} \tag{27}$$

(where V is in electrostatic units and V' is in volts), we see that the numerical constant in equation (25) should be equal to the multiplier of V' in equation (27). That is, we should have

$$\frac{e}{300h} = 2.43 \times 10^{14}$$

from which, taking $e = 4.774 \cdot 10^{-10}$ e.s.u.,

$$h = 6.55 \cdot 10^{-27}$$

in exact agreement with the value of Planck's constant h determined by other methods.

This identity in numerical values of h points to the general correctness of the explanation, on the basis of the quantum theory, of the cutoff points a, b, c . . . of the energy-distribution curves in Fig. 141 as well as of equation (26). In fact, measurements of the maximum frequency ν_m for given voltages V applied to the X-ray tube have yielded some of the most dependable values of h. Some of these values determined in this way are given in Table V.

TABLE V.—VALUES OF PLANCK'S CONSTANT h DETERMINED FROM THE LIMITING WAVE LENGTH IN THE CONTINUOUS X-RAY SPECTRUM

Investigators	Target used	h, erg-sec.
Duane and Hunt[1]	Tungsten	6.50×10^{-27}
Webster[2]	Rhodium	6.55
Blake and Duane[3]	Tungsten	6.556
Ulrey[4]	Tungsten	6.54
Wagner[5]	Various	6.52

[1] *Phys. Rev.*, vol. 6, p. 166 (1915).
[2] *Phys. Rev.*, vol. 7, p. 599 (1916).
[3] *Phys. Rev.*, vol. 10, pp. 93, 624 (1917).
[4] *Phys. Rev.*, vol. 11, p. 401 (1918).
[5] *Physik. Z.*, vol. 21, p. 621 (1920).

(*b*) *Total Intensity and Distribution of Intensity.*—Determinations of the total intensity of, and of the distribution of intensity in, the continuous X-ray spectrum are by no means so satisfactory as are the measurements of minimum wave lengths. This is due to the fact that numerous troublesome corrections have to be made to the *observed* energy-distribution curves, such as those shown in Fig. 141, before the true curve can be obtained.[1] Among these necessary corrections may be mentioned the following:

1. *The variations with wave length of the absorption of the radiation in its path from the atom of the target in which the radiation originates to the ionization chamber* where the intensity of the radiation is measured. This path includes the material of the target itself, since the X-rays originate at finite (though very small) depths below the surface; the walls of the X-ray tube and the window of the ionization chamber; and the air between the tube and the chamber.
2. *The reflecting power of the crystal grating.* This varies with wave length.
3. *Incomplete absorption in the ionization chamber.* Either an ionization chamber of sufficient length to absorb the entire X-ray beam must be used, or else corrections must be made for variation with wave length of the absorption within the chamber, since the *observed* ionization current is proportional to the energy *absorbed* in the chamber.

[1] These corrections, however, in no wise affect the determination of minimum wave lengths.

4. *"Second order" reflection.* According to equation (20), which may take the form

$$\lambda = 2d\frac{\sin\theta}{n},$$

when the crystal in the spectrometer (Fig. 136) is set at a given angle θ, a *series* of wave lengths λ will be reflected for different values 1, 2, 3, . . . of n, *provided* those several wave lengths are present in the incident radiation. Suppose, for example, that when the voltage applied to the X-ray tube is 50 kilovolts, the crystal is set at such an angle $\theta_{0.6}$ as to give a *first order* reflection (*i.e.*, $n = 1$) of $\lambda = 0.6$ Ångström. According to Fig. 141, the minimum wave length present in the X-ray spectrum generated by 50 kilovolts is 0.250 Ångström. Under these conditions, there will be reflected into the ionization chamber the *second order* wave length $\lambda = 0.3$ Ångström, in addition to the first-order wave length $\lambda = 0.6$ Ångström. The *observed* intensity when the spectrometer is set at $\lambda = 0.6$ Ångström is, therefore, due to the 2 wave lengths. For an applied voltage of 30 kilovolts, only first-order reflection is present at $\theta_{0.6}$, and no correction is necessary.

Without discussing the methods of making these several corrections,[1] the final results may be summarized as follows:

(*a*) The total radiation, *i.e.*, the area under the (corrected) energy-distribution curves, is, for a given target material and tube current, very nearly proportional to the square of the applied voltage.

(*b*) At a given voltage and tube current, the total radiation varies as the first power of the atomic number of the target.

(*c*) The wave length λ_m at which a given energy-distribution curve attains its maximum energy is given, to a rough approximation, by the relation

$$\lambda_m = 1.5\lambda_0$$

where λ_0 is the wave length at which the same curve meets the wave-length axis.

[1] See KIRKPATRICK, P.: *Phys. Rev.*, vol. 22, p. 414 (1923).

(*d*) Wagner and Kulenkampff[1] give the following empirical formula for the intensity I_ν of the X-ray energy at frequency ν from a target of atomic number Z when bombarded by electrons which have fallen through a potential V:

$$I_\nu = CZ(\nu_0 - \nu) + BZ^2$$

where ν_0 is the maximum frequency determined by the quantum relation $Ve = h\nu_0$, and C and B are constants independent of voltage and target material. This formula is in approximate agreement with a formula deduced by Kramers[2] cn theoretical grounds.

Except for determinations of minimum wave lengths, however, and the resulting law

$$h\nu_m = Ve$$

our knowledge of the *continuous* X-ray spectrum is in a very unsatisfactory state. The problem is a difficult one, whether approached from the theoretical or the experimental side, and much work remains to be done to bring this phase of X-rays up to the level of other branches of the subject.

11. The Empirical Laws of the Absorption of X-rays.—In contrast with the apparently chaotic state of affairs attending the absorption of light of the visible or near-visible portions of the spectrum, one finds comparative simplicity in the empirical laws of the absorption of X-rays. Measurements of absorption coefficients are readily made by use of the ionization spectrometer (Fig. 136(*a*)). For a given crystal angle θ and, therefore, wave length λ, the ionization current is measured both without and with a sheet of absorbing material of known density ρ and thickness x placed in the path of the beam, say between the two slits S_1 and S_2. These measurements give, respectively, I_0 and I of equation (3)

$$I = I_0 e^{-\frac{\mu}{\rho}\rho x} \qquad (3)$$

from which the mass absorption coefficient μ/ρ may be computed. In this way, being careful to use such a voltage applied to the X-ray tube as to eliminate "second order" reflections,[3] one may

[1] *Ann. Physik*, vol. 68, p. 369; and vol. 69, p. 548 (1922).

[2] *Phil. Mag.*, vol. 46, p. 836 (1923).

[3] See p. 496.

obtain values of μ/ρ for various wave lengths and various substances.

Figure 143 shows, to approximate scale,[1] the mass absorption coefficients of lead in the wave-length range $0.1 < \lambda < 1.2$ Ångströms. Beginning at point o, in the neighborhood of 0.1 Ångström, μ/ρ rises rapidly with increasing wave length until point a, corresponding to $\lambda = 0.138$ Ångström and $\mu/\rho = 8$

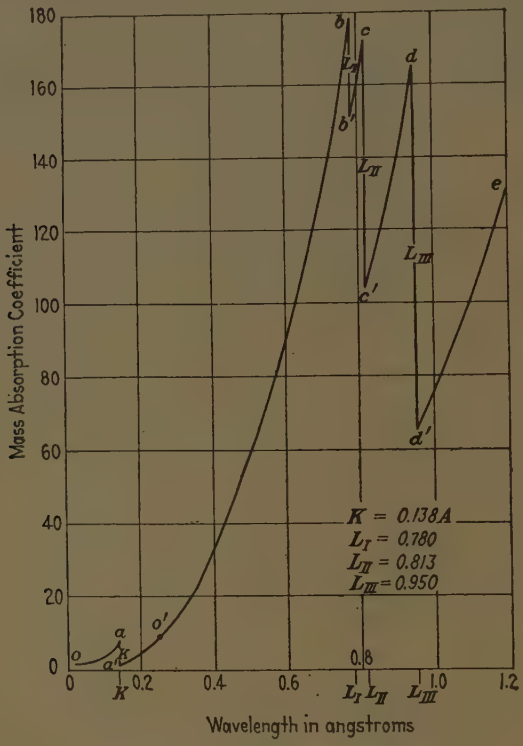


FIG. 143.—K and L absorption limits.

(about) is reached, at which occurs a sudden drop in the value of μ/ρ to point a'. With further increase in wave length, the absorption increases rapidly again, until point b, corresponding to $\lambda = 0.780$ Ångström, is reached, at which occurs another drop in the absorption coefficient to point b'. Similar "drops" or "breaks" occur at cc' corresponding to $\lambda = 0.813$ Ångström,

[1] The abscissæ represent wave lengths accurately, but the ordinate scale is only approximate.

and at dd', corresponding to $\lambda = 0.950$ Ångström. Beyond point d', the absorption again increases rapidly. If we could follow, by direct measurement, the absorption beyond point e, we should find that in the region $3.2 < \lambda < 5.0$ Ångströms, a group of *five* such "breaks" occur. Still beyond these, beginning at about 14 Ångströms, comes another group of *seven* "breaks."

These breaks, or discontinuities, are called, respectively, K, L, M . . . discontinuities, because of their intimate connection with the K, L, M . . . series of characteristic X-ray lines. There is *one* K discontinuity—aa'. There are *three* L

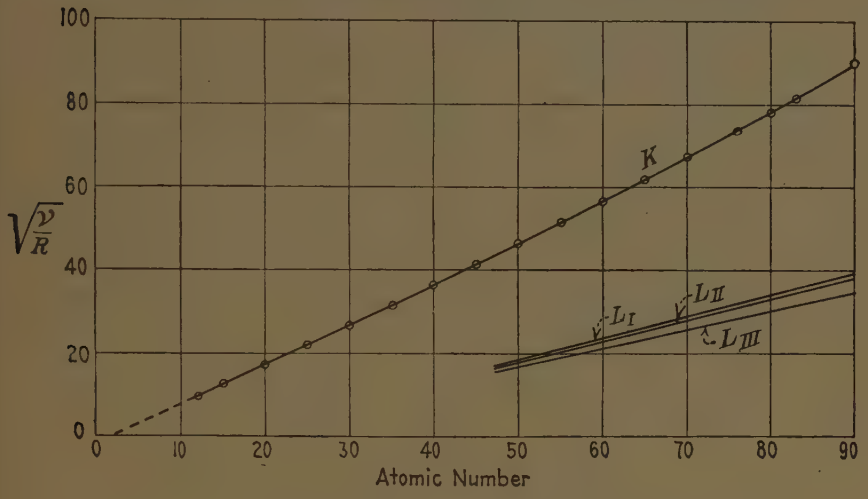


FIG. 144.—The Moseley diagram for the K and L absorption limits.

discontinuities—L_I, L_{II}, and L_{III} at, respectively, bb', cc', dd'; there are *five* M discontinuities; and so on.

Curves *exactly similar* to Fig. 143 are obtained for the absorption of X-rays in other substances, the respective discontinuities or "limits" occurring at longer wave lengths the lower the atomic number of the absorber. In fact, a curve plotted between the square root of the frequency of a given limit and atomic number is nearly a straight line similar to Moseley's curve (Fig. 140) for line spectra. Such a curve for the K limit, from Mg ($Z = 12$) to Th ($Z = 90$) is shown[1] in Fig. 144, in which, as ordinates, are plotted $\sqrt{\nu/R}$, where R is the Rydberg constant.

[1] Data from SIEGBAHN: "The Spectroscopy of X-rays," pp. 137 and 141.

$\left(\text{Obviously, } \sqrt{\frac{\nu}{R}} \propto \sqrt{\nu}.\right)$ The graph is seen to be nearly, but not quite, a straight line. For comparison, there are also shown, in Fig. 144, the corresponding graphs for the L_{I}, L_{II}, and L_{III} limits from Ag ($Z = 47$) to Th ($Z = 90$).

Not only is there regularity in the wave lengths of the absorption limits from one element to another, but there is also a remarkable regularity in the *magnitude* of the mass absorption coefficient, from wave length to wave length in a given element, and from one element to another. Figure 145 shows, to a much

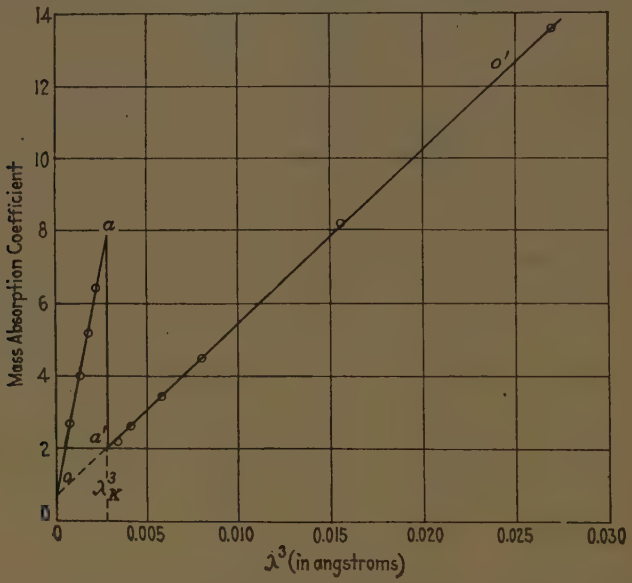


FIG. 145.—Mass absorption coefficients of lead as a function of wave length, showing the K discontinuity and the linear relation between μ/ρ and λ^3.

larger scale, the mass absorption coefficients of lead[1] in the region o to o' of Fig. 143, plotted as a function of the *cube* of the wave length. The two parts of the graph on each side of the K absorption limit aa' are seen to be *straight* lines with very nearly equal intercepts of about $\mu/\rho = 1$ on the axis of ordinates. We may, accordingly, write the empirical equation for the variation of μ/ρ with λ in the region oa as

$$\frac{\mu}{\rho} = k\lambda^3 + b \qquad (28a)$$

[1] Data taken by the author, *Phys. Rev.*, vol. 27, p. 1 (1925).

and for the region $a'o'$,

$$\frac{\mu}{\rho} = k'\lambda^3 + b \tag{28b}$$

where k and k' are the slopes of the respective lines and b is a constant. To a first approximation,[1] the mass absorption coefficient for a given absorber is a linear function of the cube of the wave length, due regard being had to the spectral region in which the equations (28) apply. The constant b is, in part at least, determined by *scattering*, and it is frequently assumed that

$$b = \frac{\sigma}{\rho}$$

where σ/ρ is the mass *scattering* coefficient. Equations (28) are frequently written in the form

$$\frac{\mu}{\rho} = k\lambda^3 + \frac{\sigma}{\rho} \tag{29}$$

A quantity of more fundamental significance than *mass* absorption coefficient μ/ρ is the *atomic* absorption coefficient μ_a. This is obtained by dividing the mass absorption coefficient, which is expressed in grams as the unit of mass, by the number of atoms per gram, N_0/A, where N_0 is Avogadro's number and A is the atomic weight, *i.e.*,

$$\mu_a = \frac{\mu/\rho}{N_0/A}$$

Dividing equation (29) through by N_0/A, we have

$$\mu_a = k_a\lambda^3 + \sigma_a \tag{30}$$

where $k_a \equiv \dfrac{k}{N_0/A}$ and σ_a is the atomic *scattering* coefficient. The term $k_a\lambda^3$ is sometimes abbreviated to τ_a, so that

$$\mu_a = \tau_a + \sigma_a$$

For reasons which will appear in Sec. 14, *infra*, τ_a is called the "fluorescent" absorption coefficient.

An equation of the type of equation (30) is applicable to the atomic absorption coefficients of all substances on the short-wave-length side of, and for a limited region beyond, their respective K absorption limits λ_K. Further, k_a varies in a perfectly

[1] There are slight systematic departures from the λ^3 law. See RICHTMYER, F. K.: *Phys. Rev.*, vol. 18, p. 13 (1921); also, ALLEN, S. J. M.: *Phys. Rev.*, vol. 27, p. 266 (1926).

systematic way with the atomic number of the absorber. It has been shown[1] that k_a is proportional to the fourth power[2] of the atomic number, *i.e.*,

$$k_a = KZ^4$$

from C ($Z = 6$) to Pb ($Z = 82$), K being a proportionality constant. Accordingly we may write as an empirical equation for the atomic absorption coefficient μ_a of X-rays of wave length λ in an absorber of atomic number Z,

$$\mu_a = KZ^4\lambda^3 + \sigma_a \tag{31}$$

On the short-wave-length side of the K absorption limit, the value of K is about $2.25 \cdot 10^{-2}$, where λ is expressed in centimeters. For a considerable range beyond the K limit on the long-wave-length side, the value of K is about $0.33 \cdot 10^{-2}$.

This systematic variation of the absorption of X-rays with atomic number Z and wave length λ, as expressed empirically by the comparatively simple equation (31), has prompted numerous theoretical investigations in which attempts have been made to derive a formula of the type of equation (31) from fundamental concepts. A summary, even, of these theoretical studies is quite beyond the scope of this book, but we shall make brief reference to the subject later (p. 513), after we have discussed the relation of the absorption of X-rays to the emission of the characteristic X-ray spectra, to which latter subject we shall now turn.

12. Characteristic X-ray Spectra.—Immediately following the work of Bragg and of Moseley, discussed in Secs. 8 and 9, above, the technique of X-ray spectrometry developed rapidly. Many new characteristic lines were soon discovered, and, at the present time, practically the entire X-ray spectrum of each element has been mapped out. Following the notation of Barkla, Bragg, and Moseley, these lines are classified into groups, respectively; $K, L, M, \ldots$ The K group consists of four principal lines known, in order of increasing wave length, as $K\gamma$, $K\beta$, $K\alpha_1$, and $K\alpha_2$. In Table VI are given the wave lengths of these four lines for several representative elements. For comparison, the

[1] RICHTMYER, F. K., and WARBURTON, F. W.: *Phys. Rev.*, vol. 22, p. 539 (1923).

[2] This "fourth power" law was first proposed by BRAGG and PIERCE, *Phil. Mag.*, vol. 28, p. 626 (1914).

TABLE VI.—WAVE LENGTHS IN ÅNGSTRÖMS OF THE K LINES OF SOME REPRESENTATIVE ELEMENTS

Element		γ	β	α_1	α_2	λ_K
S	16	.....	5.0213	5.3609	5.3637	5.0123
Ca	20	.....	3.0834	3.3517	3.3549	3.0633
Fe	26	1.7406	1.7527	1.9323	1.9365	1.7377
Zn	30	1.2810	1.2926	1.4321	1.4359	1.2963
Br	35	0.9183	0.9308	1.0376	1.0416	0.9197
Mo	42	0.6197	0.6314	0.7078	0.7121	0.6184
Ag	47	0.4861	0.4965	0.5582	0.5626	0.4850
I	53	0.3748	0.3834	0.4325	0.4370	0.3737
W	74	0.1790	0.1842	0.2088	0.2135	0.1781
Pb	82	0.1412	0.1461	0.1652	0.1700	0.1385
U	92	0.1084	0.1119	0.1264	0.1309	0.1075

wave lengths λ_K of the K absorption limits are shown in the last column. It is to be noted that, in each case, the wave length of the K limit is *slightly* less than the wave length of the gamma line.

That these four lines of the K group, or series, are intimately connected with each other and with the K absorption limit is readily shown by considering the voltage which must be applied to the X-ray tube to generate the lines. Referring to the curves shown in Fig. 141 for the energy distribution in the continuous spectrum of tungsten, it is seen that these curves show no such characteristic "humps" as were observed by Bragg and are shown in Fig. 139. As the voltage applied to the tube is raised, however, the minimum wave length λ_0 moves toward shorter wave lengths, according to the law given in equation (26): $h\nu_m = Ve$. Now, it is found that when the voltage applied to the X-ray tube has been raised to such a value that $\lambda_0 = \lambda_K$, *all four lines of the K series are simultaneously produced*, and with further increase in applied voltage, *these four lines all increase in intensity at exactly the same rate*. In the case of tungsten, for example, for which $\lambda_K = 0.1781$ Ångström, by use of equation (27) (or of the equation $\lambda = 12{,}345/V$ Ångströms, on p. 387), we find that $\lambda_0 = \lambda_K$ when the applied voltage is 69,300 volts. When higher voltages are applied to a tungsten-target X-ray tube, all the four lines of the K series of tungsten appear. The lines are absent for lower voltages, even though the applied voltage be such that λ_0 is *greater* than the wave length of the $K\alpha$ lines. From the values of λ_K, given in Table VI, one can calculate at once the voltage necessary to generate the K series of lines of the several elements.

A further, and still more intimate, relation between the K series of lines and the absorption limits is shown by considering the frequencies[1] of the lines and the limits. In columns two and

TABLE VII.—RELATION OF THE FREQUENCIES OF THE $K\alpha$ LINES OF TUNGSTEN TO THE FREQUENCIES OF THE K AND L ABSORPTION LIMITS

Absorption limit				Emission lines		
	λ, Ångströms	$\frac{\nu}{R}$	$\left(\frac{\nu}{R}\right)^{L} - \left(\frac{\nu}{R}\right)^{K}$		λ	$\frac{\nu}{R}$
K	0.17806	5,116.8				
L_{I}	1.024	889.9	4,226.9	$K\alpha_3$(?)	missing	
L_{II}	1.0726	849.6	4,267.2	$K\alpha_2$	0.21352	4,267.8
L_{III}	1.2136	750.9	4,365.9	$K\alpha_1$	0.20885	4,366.3

three of Table VII are shown the wave lengths and the values of ν/R for, respectively, the K, L_{I}, L_{II}, and L_{III} absorption limits of tungsten.[2] In column four is shown the differences in ν/R values between the K limit and each of the three L limits. The second part of the table shows the directly observed values of λ and of ν/R for the $K\alpha_1$ and the $K\alpha_2$ lines of tungsten. It is seen that the *observed value of ν/R for the $K\alpha_1$ line is almost exactly equal to the difference between the value of ν/R of the K limit and that of the L_{III} limit.* Similarly, the ν/R value of the $K\alpha_2$ line is equal to the difference between the value of ν/R of the K limit and that of the L_{II} limit. (There is, however, no known emission line which corresponds to the difference between ν/R of the K limit and that of L_{I}. We shall make mention of this later.) Putting this relation in symbols, we have (the notation is obvious)

$$\left(\frac{\nu}{R}\right)_{K\alpha_1} = \left(\frac{\nu}{R}\right)_{K} - \left(\frac{\nu}{R}\right)_{L_{\text{III}}} \tag{32a}$$

$$\left(\frac{\nu}{R}\right)_{K\alpha_2} = \left(\frac{\nu}{R}\right)_{K} - \left(\frac{\nu}{R}\right)_{L_{\text{II}}} \tag{32b}$$

[1] In part to avoid writing the large numbers required to give frequencies, the frequency ν is usually divided by the Rydberg constant R, giving ν/R. This quantity is proportional to frequency, since R is a constant. It is to be pointed out that the symbol, namely R, which, in accordance with current practice, we have here used for the Rydberg constant, differs from that used in preceding chapters.

[2] Data from SIEGBAHN, *loc. cit.*

Or, expressed in frequencies ν,

$$\nu_{K\alpha_1} = \nu_K - \nu_{L_{III}} \qquad (32'a)$$

$$\nu_{K\alpha_2} = \nu_K - \nu_{L_{II}} \qquad (32'b)$$

Equations (32′) are exactly analogous to the equations which we discussed in Chap. IX, for the lines of a spectral series. In these equations for a spectral series, the *frequency* of a line, ν, is given by the *difference* between two *terms*, or quantities, which themselves, as was pointed out, must have the dimensions of frequency. Similarly, the quantities ν_K, $\nu_{L_{II}}$ and $\nu_{L_{III}}$ of equations (32′) may be thought of as X-ray *terms*, the differences between which give the frequencies of X-ray emission lines. In the series of lines in the visible and the ultra-violet part of the spectrum, the existence of these *terms* was, in general, inferred from the relations between the lines. In the X-ray case, *the existence of the terms is made directly evident from the absorption limits*, such as are shown in Fig. 143.

This illustration, showing that the frequencies of the $K\alpha$ lines are related to the K and L absorption limits, leads to a law of far-reaching importance in X-ray spectra: *The frequencies of X-ray lines are given by the differences between the frequencies of absorption limits.* By means of this principle, it is possible, step by step, from the observed data on X-ray lines and limits, to build up the whole scheme of X-ray spectra and absorption limits. For example, the frequency of the $K\beta$ line should be given by the difference between the frequency of the K absorption limit and that of some other limit, the frequency of which we can determine from the known frequency of the $K\beta$ line and that of the K limit, thus

$$\nu_{K\beta} = \nu_K - \nu_M$$

where ν_M is the unknown frequency. The value (Table VII) of ν/R for $K\beta$ is 4,942.9. Subtracting this from the value of ν/R for the K limit, namely, 5,116.8, gives for ν_M the ν/R value 173.9, corresponding to a wave length of approximately 5.2 Ångströms. We should, therefore, expect to find an absorption limit in tungsten in the neighborhood of 5.2 Ångströms. It is difficult to make *direct* measurements of absorption coefficients at that wave length, but the existence of limits in this region is readily demonstrated by indirect means: the differences between lines in the L series and the L limits give M limits in the same way

that the differences between the $K\alpha$ lines and the K limit give L limits.

The L series contains some 25 or 30 lines designated, in an exceedingly chaotic notation, by α, β, or γ, with various subscripts $_{1, 2, 3 \ldots}$ The wave lengths and ν/R values of some of these lines are given in Table VIII. (The reason for the grouping into the three columns L_{I}, L_{II}, and L_{III} will appear presently.)

TABLE VIII.—WAVE LENGTHS AND ν/R VALUES OF SOME OF THE LINES IN THE L SERIES OF TUNGSTEN

L_{I}			L_{II}			L_{III}		
Line	λ	ν/R	Line	λ	ν/R	Line	λ	ν/R
β_4	1,299	701.7	η	1,418	642.8	l	1.675	544.0
β_3	1,260	723.2	β_1	1,279	712.4	α_2	1,484	617.8
γ_2	1,066	855.0	γ_5	1,129	807.0	α_1	1,473	618.5
γ_3	1,060	860.0	γ_1	1,096	831.8	β_2	1,242	733.8
γ_4	1,026	887.8	γ_6	1,072	850	β_5	1,212	751.6
Limit		889.9	Limit		850	Limit		751

Recalling, from above, that by combining ν_K with $\nu_{K\beta}$, an "M" absorption limit was predicted in the neighborhood of $\nu/R = 173.9$, we observe that by subtracting from the L_{I} limit $\nu/R = 889.9$ the ν/R values of the β_4 and β_3 lines in the table, we get ν/R values of 188.2 and 166.7, respectively. These are two more terms—M terms, or levels—in the spectrum of tungsten. The term 173.9 predicted from the $K\beta$ line is, therefore, really *two* terms.[1] Similarly, we get two more terms, namely, 207 and 138, by combining the L_{II} limit with the lines η and β_1. The combination of the L_{III} limit with l and α_2 gives the terms 207 and 133, the former of which is the same as the com-

[1] For, turning the procedure around, by subtracting these two limits from the K limit of tungsten $\nu/R = 5{,}116.8$, we should predict *two* lines in the K series, the ν/R values of which should be 4,928.6 and 4,950.1. The value of ν/R given above for the $K\beta$ line, namely, 4,942.9, falls between these two, which suggests that the $K\beta$ line, originally thought to be a single line, is really a close doublet. Such actually proves to be the case, as recent measurements of the $K\beta$ line of some of the lighter elements show. For example, Allison and Armstrong (*Phys. Rev.*, vol. 26, p. 701 (1925)) find that the molybdenum $K\beta$ line consists of two components, the respective wave lengths of which are 0.631571 and 0.631009 Ångströms.

bination $L_{II} - \eta$. We therefore have *five* terms of limits—they are called M limits—which we arrange in descending order of ν/R, as follows:

	ν/R	λ, ÅNGSTRÖMS
M_I.....	207	5.30
M_{II}.....	187	5.85
M_{III}.....	167	6.55
M_{IV}.....	138	7.95
M_V.....	133	8.25

These are the *five* M absorption limits in the *X-ray spectrum of tungsten.*[1] In a similar way, it is found that there are *seven* N limits. *A very large number of the observed lines in X-ray spectra can be accounted for by suitable combinations of these K, L, M . . . limits.* The K series of lines results from combinations between the K limits and the limits L, M, N . . . of lower frequency. The L series of lines results from combinations between one or the other of the L limits and limits M, N . . . of lower frequency; and so on.[2]

Some lines, however, which might be predicted on the basis of this principle of the combination of limits are not found. We have seen one example of this in Table VII: there is no line corresponding to the combination $K - L_I$. Similarly, there is no line corresponding to $L_I - M_V$; or to $L_{II} - M_{II}$. Of the 15 mathematically possible combinations between the three L limits and the five M limits, only *seven* result in actual lines. The remainder are "ruled out" by a selection principle, similar to that operating in optical spectra, to which we shall make reference in the next section.

[1] It is noted that if differences be taken between the L limits and the other L-series lines shown in Table VIII, much smaller quantities than those obtained for the M limits result. For example, $L_I - \gamma_3$ gives 29.9; $L_{II} - \gamma_1$ gives 18; etc. These are the N absorption limits.

The value 173.9 obtained by the combination $K - K\beta$ is a mean value between the M_{II} and M_{III} limits and is not a separate M limit.

[2] Lines accounted for in this way are frequently called "diagram lines," since they fit into the energy-level diagram discussed in Sec. 13. Associated with many of these diagram lines are found fainter lines which appear to be satellites of the diagram lines, and which do not fit into the energy-level diagram shown in Fig. 146. For a discussion of these satellites (also called "non-diagram lines" or "spark lines"), see Sommerfeld: "Atomic Structure and Spectral Lines;" also Robinson, Phil. Mag., vol. 4, p. 763 (1927).

13. X-ray Energy-level Diagrams.—(*a*) With the empirical data of X-ray spectra, presented in the preceding section, now before us we are in position to combine Moseley's conclusion (Sec. 9) regarding the origin of the $K\alpha$ line[1] with the concept of the arrangement of electrons in atoms, discussed at the end of Chap. XI, to explain the origin of the X-ray spectral lines.

Moseley concluded, from an application of Bohr's theory, that the $K\alpha$ line arises from the electron jumps from orbits of quantum number $n = 2$ to orbits of quantum number $n = 1$. We saw, in Chap. XI, that the electrons in the normal atom occupy various orbits characterized by total quantum numbers 1, 2, 3 . . . There are, in the heavier atoms at least, 2 electrons in orbits of quantum number $n = 1$; there are 8 electrons in orbits of quantum number $n = 2$; for $n = 3$ there are 18 electrons. The 8 L electrons (see Appendix II) are divided into three subgroups; the 18 M electrons, into five subgroups, the subgroups being characterized by certain azimuthal quantum numbers k and inner quantum numbers j. Each of these subgroups corresponds to a definite energy level within the atom. Likewise, we have seen that, because of the part which they play in the origin of X-ray lines, the absorption limits K, L_{I}, L_{II} . . . must represent *energy levels* within the atom. Bohr's theory suggests an intimate connection between these observed absorption limits or energy levels and the several groups of electrons: The two most strongly bound electrons are in the K level and are called K electrons. The next higher energy level, the 2_{11} level, contains 2 electrons and obviously corresponds to the L_{I} absorption limit. Then comes the 2_{21} level, with 2 more electrons, corresponding to the L_{II} limit. The 2_{22} level, with 4 electrons, completes the "L shell" and corresponds to the L_{III} absorption limit. Continuing in this way, the various M and N absorption limits are identified with the several n_{kj} groups of electrons, as shown in Appendix II. The absorption limits are thus characterized by the various quantum numbers n_{kj} of the electron groups with which they are respectively associated. For example, the L_{II} limit has quantum number 2_{21}; the M_{IV} limit has quantum number 3_{32}; and so on.

[1] The resolution in Moseley's apparatus was not sufficient to separate the components α_1 and α_2 of the $K\alpha$ line, which was later shown to be a doublet.

We can now construct an energy-level diagram, exactly analogous to the corresponding diagrams for optical spectra (Figs. 102 and 103), to show the origin of the lines in X-ray spectra. Figure 146 shows such a diagram for the X-ray spectrum of uranium ($Z = 92$), the energy levels K, L, M, N and O being plotted to a logarithmic scale, as in Figs. 102 and 103.

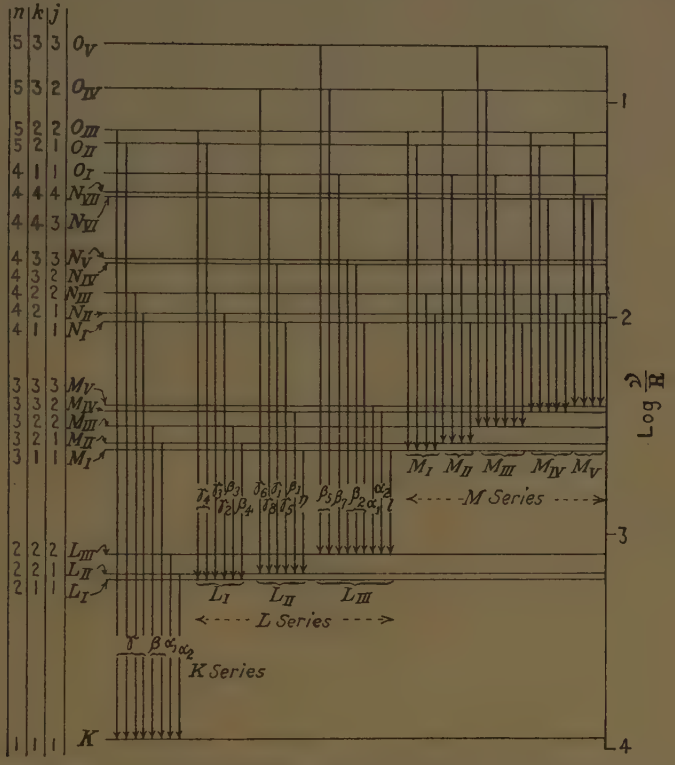


FIG. 146.—The X-ray energy-level diagram for uranium showing the complete scheme of X-ray spectra.

The three columns of figures at the left of the diagram give the n_{kj} designation of the various levels. The vertical lines indicate the lines of the K, L, and M series.

A selection rule similar to that mentioned in Chap. X is also in operation here, namely: Only those interlevel transfers are possible for which

$$\Delta k = \pm 1$$
$$\Delta j = \pm 1 \text{ or } 0$$

where Δk and Δj represent the changes in the quantum numbers k and j from the initial level to the final level. It is seen that this principle[1] "rules out" such transfers as $L_{\text{I}} \rightarrow K$, $M_{\text{I}} \rightarrow L_{\text{I}}$, etc. Transfers from both levels L_{II} and L_{III} to K are possible. These two give rise to the "doublet" $K\alpha_1$ and $K\alpha_2$. Similarly, the $K\beta$ line, which results from transfers from M_{II} and M_{III} to K, should be a doublet, a close doublet, since the levels M_{II} and M_{III} are close together when compared to the energy of the K level. Likewise, the transfers from N_{II} and N_{III} to K yield a doublet, as do also the transfers from O_{II} and O_{III}. These last four lines are so close together that they cannot be resolved, and, together, they constitute the $K\gamma$ line as *observed*.

(*b*) We can now elaborate somewhat the picture, suggested at the end of Sec. 9, of the process of the production of X-ray lines. Considering the lines of the K-series, which are produced by electrons falling from outside levels into the K level, it is obvious that before such transfers as give rise to the K lines can occur, a vacant place must *first* be made in the K shell, since this shell can contain 2, *and only* 2, electrons. To accomplish the removal of one of the K electrons requires that the atom shall be given sufficient energy, by some process, to remove that electron *to infinity, since, in the normal atom, there are no vacant places (orbits) between the K shell and the outside of the atom.* Once there is a vacant place in the K shell, the place may be filled by electrons dropping from *any* one of the outside orbits, subject to the limitations of the selection principle, into the K orbit. The totality of such transfers in a large number of atoms gives rise to the entire K series. The relative intensities of the lines are governed by the relative probabilities of transfer from the various outside orbits to the K orbit. These probabilities are determined, *in part*, by the relative numbers of electrons in the several orbits. For example, since there are twice as many electrons in the L_{III} level (4 electrons) as in the L_{II} level (2 electrons), it may be expected that the chance that an electron will drop from the L_{III} level to a vacancy in the K shell is about

[1] The quantum numbers k and j as here used for the selection rule in X-ray spectra are, so far as the *rule* is concerned, similar to the corresponding numbers in optical spectra. Sommerfeld, however ("Atomic Structure and Spectral Lines"), in applying the doublet-separation law (equation (83), Chap X) in explaining X-ray doublet separations, such as $K\alpha_1 - K\alpha_2$, identifies j with the *azimuthal* quantum number. For discussion of this point, see ANDRADE, "The Structure of the Atom," Chap. XIII.

twice as great as the chance of a similar transfer from the L_{II} level. The $K\alpha_1$ line should be *twice* as intense, therefore, as the $K\alpha_2$ line. This is found experimentally to be the case.

Only if the energy Ve of the electrons which strike the target is greater than $h\nu_K$, where V is the potential difference applied to the tube and ν_K is the frequency of the K absorption limit, can the removal of an electron from the K level take place. This is simply another way of stating the experimental result, mentioned in Sec. 10, that the K series of lines is produced only when the voltage applied to the X-ray tube is such that the minimum wave length of the continuous spectrum becomes less than the K absorption limit of the material of the target.

(*c*) As one proceeds from uranium (for which Fig. 146 was constructed) toward elements of lower atomic number, the electron groups of higher quantum numbers progressively disappear (see Appendix II), and therewith, also, the corresponding energy levels as well as the X-ray lines originating from these levels. In copper, for example, there are no O levels and only one N level. One should not expect to find, therefore, in the X-ray spectrum of copper such lines (see Fig. 146 for their origin) as $L\beta_5$, $L\beta_7$, $L\gamma_6$, $L\gamma_3$, etc.

14. Fluorescence and the Photoelectric Effect. (*a*) *The Absorption of X-rays.*—It was early observed that X-rays cause the photoelectric expulsion of electrons from materials onto which they are incident. According to Einstein's photoelectric equation

$$\tfrac{1}{2}mv^2 = h\nu - \omega_0$$

a beam of incident radiation of frequency ν will free photoelectrons with kinetic energy $\frac{1}{2}mv^2$ whenever $h\nu > \omega_0$ where ω_0 is the work required to free the electron from the surface radiated. We have seen in the preceding section that the work required to remove a K electron from an atom is $h\nu_K$. If, therefore, a beam of X-rays of frequency ν falls onto a substance the frequency of the K absorption limit of which is ν_K, it is to be expected that, by virtue of the photoelectric process, K electrons may be photoelectrically expelled from (some of) the atoms of the substance if

$$h\nu > h\nu_K$$

If, however,

$$h\nu < h\nu_K$$

no photoelectric emission *from the K shell* can result. This concept at once offers an explanation of the general features of the absorption curves, such as Fig. 143. Let Fig. 147 represent diagrammatically the absorption curve for a susbtance which has a K absorption discontinuity at λ_K, frequency ν_K. If radiation of wave length λ_1 and frequency ν_1 falls on a slab of the absorber, where $\nu_1 > \nu_K$, photoelectrons will be expelled from the K shell with kinetic energies given by

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_K \qquad (33)$$

Photoelectrons will come not only from the K level but also from the L, M . . . levels as well, the residual kinetic energies

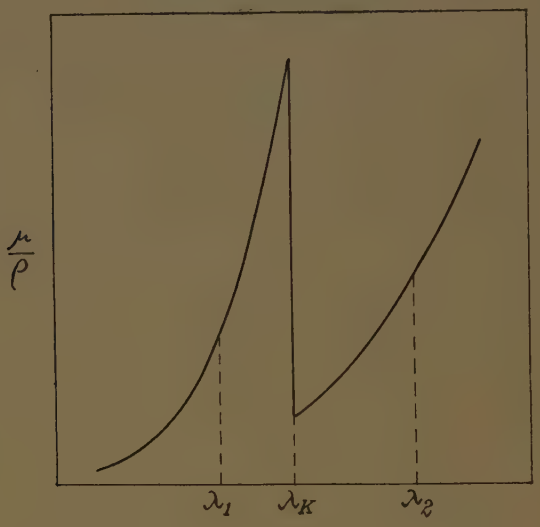


FIG. 147.

of the electrons coming from these latter levels being correspondingly greater than that of the K photoelectrons. The energy required to cause the removal of these electrons comes from the incident X-ray beam. For every electron photoelectrically expelled, whether it be a K, an L, or an M photoelectron, a *quantum of energy* $h\nu$ is removed *from the incident beam—i.e.*, due to the photoelectric process, the beam suffers *absorption* as it passes through the material.

If the incident beam of X-rays has a wave length λ_2, however, and frequency ν_2 such that $\nu_2 < \nu_K$, the incident quantum of energy is not sufficient to remove electrons from the K shell

(since $h\nu < h\nu_K$), and only L, M . . . photoelectrons will result. For *any* frequency ν of incident radiation such that $\nu > \nu_K$, there will be K, L, M . . . photoelectrons; while if $\nu < \nu_K$, there will be only L, M . . . photoelectrons. *Hence, the sudden break or discontinuity in the absorption curves at* λ_K. Excepting for scattering, practically the entire absorption of X-rays is accounted for in this way. We may, therefore, divide the absorption coefficient μ_a into two parts, *viz.*,

$$\mu_a = \tau_a + \sigma_a$$

where τ_a is the photoelectric (or fluorescent) absorption coefficient and σ_a is the scattering coefficient.

According to the curves in Fig. 143, the absorption increases rapidly as one approaches an absorption limit from the short-wave-length side. This means that the nearer the frequency ν of the incident radiation is to ν_K the more photoelectrons are expelled; or *the greater is the probability that an incident quantum will collide with an atom in such a way as to expel an electron from the atom.* It is the variation of this probability with wave length that gives rise to the *shape* of the absorption curves as expressed by the empirical equation (31):

$$\mu_a = KZ^4\lambda^3 + \sigma_a \qquad (31)$$

Partly on the basis of the general laws of probability, partly from considerations based on both quantum theory and classical physics, several investigators have derived theoretical formulæ for the atomic absorption coefficient.[1]

Of these formulæ, that of de Broglie agrees best with experiment in so far as it predicts the absolute magnitude of absorption coefficients on the short-wave-length side of the K absorption limit. The formula derived by de Broglie is

$$\tau_a = \frac{\pi e^2}{mh^2c^4}(n_K E_K^2 + n_L E_L^2 + \cdots)\lambda^3 \qquad (34)$$

where τ_a represents that part of the total atomic absorption coefficient μ_a, due to the photoelectric effect above mentioned; n_K, n_L . . . are the numbers of electrons in the K, L . . . shells (*i.e.*, 2, 8, 18 . . .); and E_K, E_L . . . stand for the

[1] COMPTON, A. H.: *Phys. Rev.*, vol. 14, p. 249 (1919); DE BROGLIE, L.: *Jour. phys.*, vol. 3, p. 33 (1922); KRAMERS, H. A.: *Phil. Mag.*, vol. 46, p. 836 (1923); OPPENHEIMER, J. R.: *Zeit. für Physik*, vol. 41, p. 268 (1927). For a discussion of these formulæ, see RICHTMYER, F. K.: *Phys. Rev.*, vol. 27, p. 1 (1925); and vol. 30, p. 755 (1927).

energy $h\nu_K$, $h\nu_L$ . . . necessary to remove an electron from the K, L . . . limit. The other quantities have meanings previously assigned to them. In using the formula, all the terms within the bracket are to be used to compute absorption coefficients τ_a on the short-wave-length side of the K limit. For the region $\lambda > \lambda_K$, the first term $n_K E_K^2$ is to be dropped; for $\lambda > \lambda_L$, the first two terms are to be dropped; and so on.

While, however, the empirical formulæ, such as equation (31), and theoretical formulæ, such as equation (43) give a close approximation to the experimental facts, these formulæ are, in fact, approximations only. The correct law of the absorption of X-rays is yet to be discovered.

(*b*) *Fluorescence.*—In the visible spectrum, the characteristic radiation emitted by a substance when radiated with light of wave length shorter than that of the characteristic radiation is called "fluorescent radiation." We have already mentioned the fluorescence of X-rays in connection with the work of Barkla (Sec. 4). The explanation of this phenomenon follows, at once, from the above discussion of the photoelectric effect. When X-rays of frequency $\nu > \nu_K$, where ν_K is the frequency of the K absorption limit, fall upon a substance, electrons may be photoelectrically expelled from any of the orbits K, L, M . . . The filling of these vacant places by electrons falling from outside orbits results in the emission of the entire characteristic spectrum of the elements. If, however, $\nu_L < \nu < \nu_K$, electrons are not expelled from the K orbits, and, accordingly, only the L, M . . . series of lines appear in the fluorescent spectrum—in accord with the observations of Barkla.

(*c*) *Direct Observation of the Photoelectric Effect of X-rays.*—These photoelectric phenomena together with the existence within the atom of the various energy levels K, L_{I}, L_{II} . . . occupied by electrons receive direct confirmation from observations of the velocities of photoelectrons expelled from a given element by X-rays of known frequency.

Let a beam of X-rays of frequency ν fall upon a substance the frequencies of the absorption limits of which are ν_K, $\nu_{L_{\text{I}}}$, $\nu_{L_{\text{II}}}$ . . . , where $\nu > \nu_K$. Photoelectrons may be expelled from any level. Because of the different amounts of energy $h\nu_K$, $h\nu_{L_{\text{I}}}$, $h\nu_{L_{\text{II}}}$ . . . needed to remove electrons from the several limits, the velocities of these photoelectrons *as they leave the atom* will not all be the same but will depend on the respective

levels from which they have originated. Thus, the velocity v_K of the photoelectrons coming from the K level is given by Einstein's equation[1]

$$\tfrac{1}{2}mv_K^2 = h\nu - h\nu_K \qquad (35a)$$

The L_{I} photoelectrons have velocity $v_{L_{\text{I}}}$, likewise given by

$$\tfrac{1}{2}mv_{L_{\text{I}}} = h\nu - h\nu_{L_{\text{I}}} \qquad (35b)$$

Since $\nu_K > \nu_{L_{\text{I}}}$, it follows that the L_{I} photoelectrons, after leaving the atom, have a greater velocity than the K photoelectrons.

Among the experiments directly confirming this conclusion are those of Robinson,[2] whose apparatus is shown diagrammatically in Fig. 148. A beam of X-rays of frequency[3] ν enters

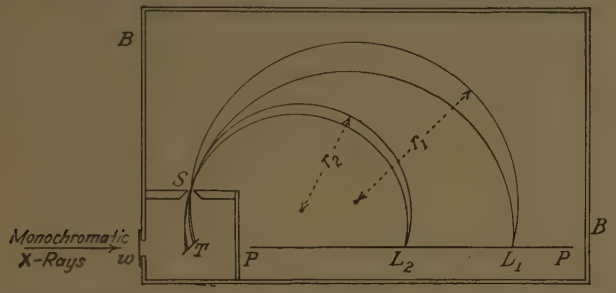


FIG. 148.—Robinson's magnetic spectrograph for studying the photoelectric action of X-rays.

through a thin window W a highly evacuated brass box BB and falls upon a target T of the material under investigation. Photo-

[1] Neglecting the change of mass with velocity. In an experiment such as Robinson's, the velocity of the electrons becomes such that variation of mass with velocity must be taken into account.

[2] *Proc. Roy. Soc.*, (London) vol. 104, p. 455 (1923); *Phil. Mag.*, vol. 50, p. 241 (1925). For previous articles on the same subject, see: ROBINSON and RAWLINSON: *Phil. Mag.*, vol. 28, p. 277 (1914); HU, K. F.: *Phys. Rev.*, vol. 11, p. 505 (1918); DE BROGLIE: *Jour. phys.*, vol. 2, p. 265 (1921); ELLIS, *Proc. Roy. Soc.*, (London) vol. 99, p. 261 (1921).

[3] It is impossible by present experimental means to get a strictly monochromatic beam of X-rays of sufficient intensity for such experiments as this. Accordingly, use is made of the fact that, with suitable exciting voltage, the $K\alpha$ lines from an X-ray target are much more intense than the accompanying radiation of the other wave lengths and, therefore, serve as a "monochromatic" beam, particularly if the beam is first passed through a filter of suitable thickness, the wave length of whose K limit is just shorter than the wave length of the $K\alpha$ lines. (See HULL, A. W.: *Phys. Rev.*, vol. 10, p. 661 (1917).)

electrons are expelled from the surface of T in all directions and with various velocities, as indicated by equations (35). The whole apparatus is placed in a known magnetic field H, at right angles to the plane of the paper. H can be varied at will. The photoelectrons will describe circles of radii r given by, neglecting the correction for change of mass with velocity,

$$Hev = \frac{mv^2}{r} \tag{36}$$

where v is the velocity of the photoelectrons moving at right angles to the field. Some of these electrons will pass through the narrow slit S and, continuing their circular path, will strike the photographic plate PP. If the electrons leaving T have velocities v_1, v_2 . . . they will move in circles of radii r_1, r_2 . . . and will strike the photographic plate at points L_1, L_2 . . . As shown in the figure, the arrangement is such as to "focus" electrons leaving the different parts of the target with the same velocity onto the plate at such positions as L_1 and L_2, the diameter of the circles being the distance between S and L_1 or L_2.

Robinson found on the plate a number of "lines" corresponding to groups of electrons of different velocities v_1, v_2, etc., the magnitudes of which could be readily determined from the position of the lines on the plate and the magnetic field H, by use of equation (36). Knowing v, the kinetic energy of each group of electrons could then be computed, giving the term $\frac{1}{2}mv^2$ in equation (35):

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_0$$

where $h\nu_0$ stands for the quantities $h\nu_K$, $h\nu_{L_I}$, $h\nu_{L_{II}}$ . . . The term $h\nu$ is known from the frequency of the incident radiation. The several values of $h\nu_0$ are, thus, at once obtainable, and from them the absorption limits ν_K, ν_{L_I}, $\nu_{L_{II}}$ . . .

This experiment gives as nearly as one could wish a *direct* method of proving (1) that electrons exist at various energy levels within the atom and (2) that the numerical evaluation of these levels by spectroscopic methods is correct, since, as Table IX shows, *Robinson's results are in complete agreement with the data of X-ray spectroscopy.* It is most remarkable that Robinson finds *one K* level, *three L* levels, *five M* levels, and, in the case of Bi ($Z = 83$), six of the seven N levels, the levels N_{VI} and N_{VII} being too close together to be resolved in his apparatus.

TABLE IX.—X-RAY ABSORPTION LIMITS DETERMINED FROM THE MAGNETIC SPECTRUM OF PHOTOELECTRONS (AFTER ROBINSON); COMPARISON WITH SPECTROSCOPIC METHOD

Level	Thorium ($Z = 90$)		Tungsten ($Z = 74$)		Silver ($Z = 47$)		Manganese ($Z = 25$)	
	Robinson	Spectroscopy	Robinson	Spectroscopy	Robinson	Spectroscopy	Robinson	Spectroscopy
K	.....	.....	.....	.....	.....	.....	480.1	484
L_{I}	.....	.....	.....	.....	280.0	280.0	55.3	57.1
L_{II}	.....	.....	.....	.....	260.1	260.4	47.9	48.8
L_{III}	.....	.....	.....	.....	246.2	247.9		48.0
M_{I}	379.5	381.5	208.5	206.8	47.1	53.4		
M_{II}	355.1	354.7	189.4	188.2		43.5		
M_{III}	297.0	298.0	167.5	166.7	39.0	41.3		
M_{IV}	258.3	256.5	139.0	137.0	23.8	27.9		
M_{V}	244.5	244.9	133.0	132.4		27.5		
N_{I}	92.8	97.9	31.4	42.9				
N_{II}	86.0	90.0		35.0				
N_{III}	69.0	71.5		30.0				
N_{IV}	48.4	56.1	17.2	17.6				
N_{V}		47.7		17.1				
N_{VI}	24.4	28.2						
N_{VII}		27.4						

(Data is given in terms of ν_0/R where ν_0 is the frequency of the limit, and R is the Rydberg constant.) The columns headed "Robinson" give Robinson's observations. Those headed "Spectroscopy" give the values of the levels as determined from X-ray spectroscopy.

15. The Scattering of X-rays; the Compton Effect.—Mention was made, in Sec. 3, that Barkla, from his measurements of the scattering coefficients, computed the number of electrons per atom by use of Sir J. J. Thomson's formula for scattering which was based on the ether-pulse (classical) theory of X-rays. This was the first unambiguous determination of the number of electrons per atom. In spite of this success, there is no phase of modern physics which better illustrates the inadequacy of classical theory than the scattering of X-rays.

(*a*) *Total Scattering Coefficients.*—According to equation (12), of Sec. 3(*b*), the mass scattering coefficient for X-rays should be

$$\frac{\sigma}{\rho} = \frac{8\pi}{3}\frac{e^4}{m^2c^4}\frac{n}{\rho} \tag{12}$$

where ρ is the density of the scattering material and n is the number of (scattering) electrons per cubic centimeter. According to this equation: (1), σ/ρ should be independent of both scattering material and wave length; and (2), the numerical value of σ/ρ should be very nearly 0.2, as may be verified by put-

ting into equation (12) the numerical values of the constants e, m, and c and the values of n and ρ for some scattering material, such as carbon or aluminum.

For the lighter scattering materials and for X-rays of moderate wave length, the scattering coefficients approximate the value required by classical theory, namely, 0.2. But for hard X-rays, say $\lambda = 0.1$ Ångström, and for some such scatterer as carbon, the *total* absorption coefficient, *scattering plus fluorescent* absorption,[1] is only 0.15; while for gamma rays, the wave length of which is of the order of 0.02 Ångström, the total absorption coefficient is, approximately, 0.06. For this latter wave length, the *scattering* coefficient must, therefore, be *less than one-third of the value required by classical theory*. Thus, not only do scattering coefficients vary with wave length, contrary to classical theory, but also the values of the coefficients for hard X-rays and gamma rays are *very much smaller* than required by equation (12).

(*b*) *The Angular Distribution of Scattered X-ray Energy.*—The ether-pulse theory of X-rays led to equation (19)

$$I'_\phi = I \frac{e^4}{m^2c^4} \frac{1}{R^2} (1 + \cos^2 \phi) \qquad (19)$$

for the intensity I'_ϕ of X-rays scattered per electron at an angle ϕ from the direction of the incident beam, the intensity of which is I. R is the distance between the scatterer and the place where the scattered energy is measured. According to this equation, the scattering should be symmetrical forward and backward about a plane passing through the scatterer and perpendicular to the direction of the incident rays. For $\phi = 0$, the value of the bracket in equation (19) is 2; for $\phi = \pi/2$, the value is 1. That is, the energy scattered in the forward direction should be twice that scattered at 90 degrees from the incident beam. The full line in Fig. 149 gives the predicted distribution for various angles from the direction of incidence, according to equation (19).

The measurements of Barkla and Ayres[2] for the scattering from carbon at various angles, using moderately soft X-rays, are shown by the small circles. The observations agree very

[1] For tables and literature references, see COMPTON, A. H., "X-rays and Electrons."

[2] *Phil. Mag.*, vol. 21, p. 270 (1911).

well with the predictions, except in the forward direction for angles *less* than 45 degrees from the incident direction. In this forward direction, the scattering is greater than predicted. For short X-rays, this dissymmetry increases, the backward scattering becoming relatively *less* with increasing frequency. For *gamma* rays, the dissymmetry becomes very great, as is shown by the dots which represent the scattering by iron of the gamma rays from radium *C* as measured by Compton.[1] In this latter case, the scattering is almost entirely in the forward direction. As in the case of the *magnitude* of the scattering coefficient, the

FIG. 149.—The angular distribution of scattered X-rays from carbon as a scatterer. The full line is the prediction of classical theory; the circles are the observations of Barkla and Ayres for moderately soft X-rays; the dots are the observations of Compton for gamma rays.

discrepancy between the classical theory increases with increasing frequency of the scattered radiation.

(*c*) *The Wave Length of the Scattered Radiation; the Compton Effect.*—If X-rays consist of wave trains of definite frequency, then a primary beam of X-rays of frequency ν incident onto a scattering material, such as carbon, aluminum, or the like, should set the electrons of the scatterer into forced vibrations with the frequency ν; and these electrons should then radiate a secondary, or scattered, beam of X-rays of the same identical frequency as the primary beam. It was early found that, in general, secondary radiation is *less* penetrating than the primary—a fact which was later explained by the presence in the secondary beam of the *characteristic fluorescent* radiation, which, as we

[1] *Phil. Mag.*, vol. 41, p. 749 (1921). These measurements are not plotted to the same scale in Fig. 149 as are those of Barkla and Ayres.

have seen above, is always of longer wave length, and, therefore, less penetrating, than the exciting primary beam. In a scattering material of very low atomic number, such as carbon, however, the fluorescent radiation is of such a *long* wave length as to be absorbed by even a thin film of air. Yet even with carbon as a scatterer, the secondary beam was found to be somewhat less penetrating, and presumably, therefore, of somewhat longer mean wave length,[1] than the primary—a fact quite inexplicable on classical theory.

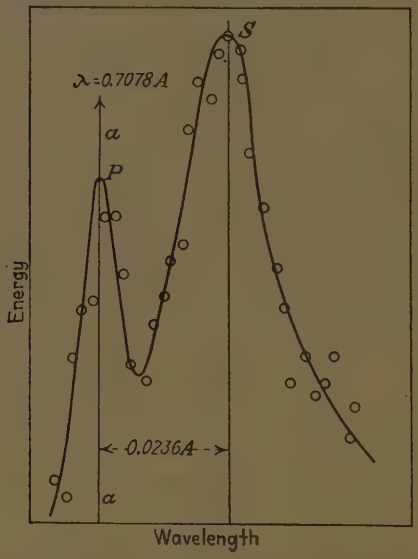


FIG. 150.—The spectrum of scattered X-rays, showing the unmodified line *P*, and the modified or "shifted" line *S* (*Compton*).

In a spectrometric investigation of scattered radiation, A. H. Compton[2] showed that when monochromatic radiation falls upon a scatterer, the scattered beam, at least from the lighter elements—lithium, carbon, aluminum—as scatterers, is composed of *two* lines, one corresponding in wave length to that of the primary beam and the other being of definitely *longer* wave length. Figure 150 shows the spectrum of scattered radiation from a carbon scatterer when irradiated by the $K\alpha$ line of molybdenum, the scattered radiation being observed at an angle of

[1] Because of the known variation of the coefficient of absorption with wave length.

[2] *Phys. Rev.*, vol. 21, p. 715; vol. 22, p. 409 (1923).

90 degrees from the incident radiation. The vertical line *aa* gives the wave length of the primary radiation. There are seen to be two maxima, or lines, one of which P corresponds *exactly* to the primary radiation; the other S is "shifted" toward longer wave lengths from the position of the primary, the difference in wave length between the *shifted* and the *unshifted* components being 0.0236 Ångström. Classical theory could not account for the presence of this shifted component. Its explanation by Compton is one of the most striking applications of the quantum theory.

Compton boldly applied the extreme quantum picture of radiant energy, according to which a beam of radiant energy consists of a stream of localized "pellets," *i.e.*, quanta, of energy of magnitude $h\nu$. These quanta, since they are in motion (with the velocity of light) and possess energy, must also possess momentum. When, therefore, they collide with material particles, such as atoms or electrons, it might be expected that the collisions would be governed by the two laws of mechanics: (1) the conservation of energy and (2) the conservation of momentum.

We must first compute the momentum of a quantum which possesses energy $h\nu$ and is moving with velocity c. Proceeding as in the computation, on the basis of the kinetic theory of gases, of the pressure produced by the molecules of a gas, we first compute the momentum which a stream of quanta, incident onto and absorbed by a surface, communicates to that surface in 1 second, since such transfer of momentum per square centimeter per second is equal to the pressure produced by the incident beam of radiation. Let I be the intensity of the incident beam of radiation, assumed monochromatic and of frequency ν. (I is the energy contained in a volume of the radiation 1 sq. cm. in cross-section and c cm. long.) The total number N of quanta, each of energy $h\nu$, contained in this volume, is, then,

$$N = \frac{I}{h\nu}$$

Let the momentum of *each* quantum be p. Since these N quanta are incident onto 1 sq. cm. of the surface in 1 second, the *total* momentum P transferred from the radiation to the surface per square centimeter per second is

$$P = \frac{I}{h\nu} p$$

But by the ordinary laws of mechanics, P is numerically equal to the *pressure* which the radiation exerts on the surface, and we saw, in Chap. VII, Sec. 6, that, *irrespective of any theory as to the nature of radiation*, the pressure exerted by radiation falling normally onto a surface is numerically equal to the energy density ψ of the radiation. Therefore, $P = \psi$ and

$$p \cdot \frac{I}{h\nu} = \psi$$

But ψ is obviously given by

$$\psi = \frac{I}{c}$$

$$\therefore p \frac{I}{h\nu} = \frac{I}{c}$$

from which it follows, at once, that

$$p = \frac{h\nu}{c} \tag{37}$$

That is, the momentun p of a quantum is obtained by dividing the energy $h\nu$ of the quantum by the velocity of light c.

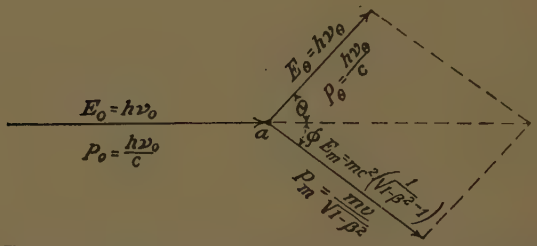


FIG. 151.—Vector diagram showing the conservation of momentum when a quantum is scattered by an electron.

Having now the energy of the quantum $h\nu$ and its momentum $h\nu/c$, we can apply to the collision between a quantum and an electron the laws of the conservation of energy and of momentum, in exactly the same way as we should solve the problem of the elastic collision of two billard balls.

Let an incident quantum, energy $E_0 = h\nu_0$ and momentum $p_0 = h\nu_0/c$, collide with an electron a (Fig. 151), mass m, and initially at rest. After the collision, the electron will move in a

direction making an angle of ϕ, say, with the initial direction of motion of the quantum, while the quantum itself will move in a direction making an angle θ with its initial direction. Qualitatively, one sees, at once, that the energy E_θ of the quantum after collision and, therefore, also the frequency, must be less than that of the quantum before collision, since some of the energy of the incident quantum must have been given to the electron if it has been set in motion.

We can now write the equations for the conservation of energy and momentum. Let

$E_0 = h\nu_0$ = the energy of the quantum before collision

$E_\theta = h\nu_\theta$ = the energy of the quantum after collision, the direction of motion making an angle θ with the initial incident direction

$E_m = mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right)$ = the kinetic energy[1] of the electron

$p_0 = \frac{h\nu_0}{c}$ = the momentum of the quantum before collision

$p_\theta = \frac{h\nu_\theta}{c}$ = the momentum of the quantum after collision

$p_m = \frac{mv}{\sqrt{1-\beta^2}}$ = the momentum of the electron[1]

$\beta = v/c$, where v is the velocity of the electron

From the law of the conservation of energy, we write,

$$E_0 = E_\theta + E_m$$

i.e.,

$$h\nu_0 = h\nu_\theta + mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) \qquad (38a)$$

[1] The theory of relativity leads to the following expression for the kinetic energy E_k of a mass m moving with velocity v:

$$E_k = mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right)$$

where $\beta = v/c$ is the ratio of the velocity of the body to the velocity of light. Our ordinary expression for the kinetic energy, *i.e.*, $\frac{1}{2}mv^2$, is the first term in the expansion of this equation and is sufficiently accurate for $\beta << 1$. Since $v = \beta c$, we may write the equation for momentum p:

$$p = \frac{m\beta c}{\sqrt{1-\beta^2}}$$

where $\frac{m}{\sqrt{1-\beta^2}}$ gives the variation of mass with velocity.

From the law of the conservation of momentum, we can write for the x-components of momentum (*i.e.*, parallel to p_0),

$$\frac{h\nu_0}{c} = \frac{h\nu_\theta}{c}\cos\theta + \frac{m\beta c}{\sqrt{1-\beta^2}}\cos\phi \qquad (38b)$$

And for the y-components,

$$0 = \frac{h\nu_\theta}{c}\sin\theta + \frac{m\beta c}{\sqrt{1-\beta^2}}\sin\phi \qquad (38c)$$

In these three independent equations, we have, given ν_0 the frequency of the incident quantum, the *four* unknown quantities ν_θ, θ, ϕ, and β. By simultaneous solution, we can obtain three of them in terms of a fourth, say θ, which is the direction with respect to the incident beam in which the quantum is "scattered" as a result of the particular collision.

To solve these equations, set

$$\frac{h\nu_0}{mc^2} \equiv \mu_0 = \frac{h}{mc\lambda_0}; \qquad \frac{h\nu_\theta}{mc^2} \equiv \mu_\theta = \frac{h}{mc\lambda_\theta}$$

where λ_0 and λ_θ are the wave lengths (whatever that may mean in terms of this "picture"!) of the incident and the scattered quantum. By slight rearrangement, equations (38) then take the following respective forms:

$$\mu_0 - \mu_\theta = \frac{1}{\sqrt{1-\beta^2}} - 1 \qquad (39a)$$

$$\mu_0 - \mu_\theta\cos\theta = \frac{\beta}{\sqrt{1-\beta^2}}\cos\phi \qquad (39b)$$

$$\mu_\theta\sin\theta = -\frac{\beta}{\sqrt{1-\beta^2}}\sin\phi \qquad (39c)$$

Squaring equation (39a) and rearranging gives equation (40); and squaring equations (39b)and (39c) and adding gives equation (41), *viz.*,

$$\mu_0^2 + \mu_\theta^2 - 2\mu_0\mu_\theta + \frac{2}{\sqrt{1-\beta^2}} = \frac{1}{1-\beta^2} + 1 \qquad (40)$$

$$\mu_0^2 + \mu_\theta^2 - 2\mu_0\mu_\theta\cos\theta = \frac{\beta^2}{1-\beta^2} \qquad (41)$$

Subtracting equation (41) from equation (40) gives, by aid of equation (39a),

$$\mu_0 - \mu_\theta = \mu_0\mu_\theta(1-\cos\theta) \qquad (42)$$

$$\therefore \frac{1}{\mu_\theta} - \frac{1}{\mu_0} = (1-\cos\theta)$$

$$\therefore \lambda_\theta - \lambda_0 = \frac{h}{mc}(1-\cos\theta) \qquad (43)$$

by replacing the equivalent of μ. Putting in the numerical values of h, m, and c gives

$$\lambda_\theta - \lambda_0 \equiv d\lambda_\theta = 0.0243(1 - \cos\theta) \qquad (43')$$

where λ is expressed in Ångströms.

This important equation states that *when an incident radiation of wave length* λ_0 *is scattered at an angle* θ, *the wave length* λ_θ *of the scattered radiation should be greater than that of the incident radiation by the quantity* $0.0243(1 - \cos\theta)$, which, for a given angle θ, is constant *whatever the incident wave length.* When the scattering angle is 90 degrees, the "shift" $d\lambda_{90}$ in wave length between the primary and the scattered beam should be

$$d\lambda_{90} = 0.0243 \text{ Ångström}$$

exactly in accord with Compton's measurements, quoted on page 521. Further, the shift should be entirely independent of the material of the scatterer and for various angles θ of scattering should be proportional to $(1 - \cos\theta)$.

(*d*) These predictions have been abundantly confirmed by the investigations of Compton and his collaborators,[1] Ross,[2] J. A. Becker,[3] Allison and Duane,[4] and others. For details, the student is referred to the original articles.

By use of equations (42) and (38*a*), it is readily found that the energy E_m of the recoiling electron is

$$E_m = h\nu_0 \frac{\mu(1 - \cos\theta)}{1 + \mu(1 - \cos\theta)} \qquad (44)$$

and from the construction of the Fig. 151, it is evident that the electron must move in the forward direction, *i.e.*, $\phi < \pi/2$. Following Compton's prediction of their existence, these "recoil" electrons, as they are called, were discovered by C. T. R. Wilson[5] and W. Bothe.[6] They have been studied quantitatively by Compton and Simon[7] and others. Bless,[8] by the method of the

[1] *Phys. Rev.*, vol. 21, pp. 207, 483, 715 (1923); *Proc. Nat. Acad. Sci.*, vol. 10, p. 271 (1924).

[2] *Proc. Nat. Acad. Sci.*, vol. 9, p. 246 (1923); *Phys. Rev.*, vol. 22, p. 524 (1923).

[3] *Proc. Nat. Acad. Sci.*, vol. 10, p. 342 (1924).

[4] *Proc. Nat. Acad. Sci.*, vol. 11, p. 25 (1925); Woo, Y. H.: *Phys. Rev.*, vol. 27, p. 242 (1926).

[5] *Proc. Roy. Soc.*, (London) vol. 104, p. 1 (1923).

[6] *Zeit. für Physik*, vol. 20, p. 237 (1923).

[7] *Phys. Rev.*, vol. 25, p. 306 (1925).

[8] Dissertation, Cornell University (1927). *Phys. Rev.*, vol. 29, p. 918 (1927).

magnetic "spectrograph," similar to Robinson's method for photoelectrons, has measured the value of E_m for the recoil electrons and has found that the results are in agreement with Compton's equation (44).

The presence of the so-called "unmodified" line (P, in Fig. 150) may be accounted for as follows: In setting up equations (38), it was assumed that the mass with which the quantum collides is that of a "free" electron or, at least, that the kinetic energy E_m given to the electron by the collision is sufficient to remove the electron from an atom in which the electron may be "bound." If, however, the energy required to remove the electron is *greater* than E_m, the electron will *not* be removed from the atom, and we may regard the collision as taking place between the electron and the atom as a whole, the mass of which, M, is far greater than that of the electron. If M be substituted for m in equation (43), it is readily seen that the computed change of wave length is so small as to be quite beyond the possibility of detection. A certain proportion of collisions between quanta and the electrons of a scattering substance will involve electrons so loosely bound that they are ejected from the atom; a change of wave length in the scattered radiation then results. In other collisions, the energy given to the electron will be insufficient to remove the electron from the atom, and no change of wave length results. The scattered radiation should, therefore, contain both the shifted and the unshifted lines, exactly as Compton found. It can be shown that the relative intensities of these components should depend on the wave length of the incident radiation and on the atomic number of the scatterer. These predictions are also confirmed, qualitatively, by experiment.

(*e*) This radical picture of the quantum structure of radiation, which is so successful in explaining the Compton effect, finds curious confirmation when one computes, by the application of the same concepts, the radius of the electron from the measured value of the magnitude of the X-ray scattering coefficients. We may "explain" the phenomenon of the scattering of X-rays by assuming that *some* of the quanta of an incident beam in passing through matter are deflected from their paths by collisions with electrons, the remaining quanta proceeding through the scattering material undeviated. If the electron is a sphere of radius a, we may think of it as obstructing the free passage of quanta over an area πa^2 and that a quantum is deviated, or

scattered, whenever it hits this area. Let an incident beam of radiation be of such intensity that Q quanta per second strike a square centimeter of a thin slab of absorbing material of density ρ and thickness dx, which contains n electrons per cubic centimeter. Then the fraction dQ/Q of the Q quanta which are scattered is evidently the same as the ratio of the total projected area dA of all the electrons in the square centimeter to 1 sq. cm., *i.e.*,

$$\frac{dQ}{Q} = \frac{dA}{1} = \frac{\pi a^2 n dx}{1}$$

Proceeding exactly as in the derivation of the mass absorption coefficient in equation (2), we find that the mass scattering coefficient σ/ρ should be

$$\frac{\sigma}{\rho} = \frac{\pi a^2 n}{\rho}$$

Now, the measured value of the mass scattering coefficient for carbon is approximately 0.15. And n/ρ, the number of electrons per gram (ρ = density) of carbon, is

$$\frac{N_0}{A} Z = \frac{6.06 \times 10^{23}}{12} \times 6 = 3.03 \times 10^{23}$$

where $N_0 \equiv$ Avogadro's number, $A \equiv$ atomic weight, $Z \equiv$ atomic number. Putting these values in the above equation and solving for a, the radius of the electron, gives

$$a = 4 \times 10^{-13} \text{ cm. (about)}$$

From equation (22) of Chap. V we have another method of computing the radius of an electron on the assumptions that the electron is a sphere of radius a and mass m with its charge e uniformly distributed over the surface of the sphere—admittedly a very highly artificial concept. Then

$$m = \frac{2}{3} \frac{e^2}{ac^2}$$

Knowing m ($= 9 \times 10^{-28}$ grams) and e ($= 4.77 \times 10^{-10}$ e.s.u.), we can compute a. We find

$$a = 2 \times 10^{-13} \text{ cm. (about)}$$

Although these two values of a, *computed from absolutely dissimilar data*, are not *equal*, it is quite remarkable that they are

at least of the same *order of magnitude*. The quantity a cannot, in all probability, have the precise physical meaning which either of these two computations assign to it. Yet it is a quantity which has the dimensions of a length and is, in some way, associated with the electron. How—we must leave to future research.

Further, we may raise the question: Precisely under what circumstances does a collision between a quantum and an atom (or an electron) result in the "scattering" of the quantum, as contrasted with the circumstances under which a collision results in the photoelectric expulsion of the electron? In the former case, only a small part (or none at all) of the energy of the quantum is lost; in the latter case, the *entire* energy of the quantum disappears. It is probable that an unambiguous answer to this question can be made only after we have a much more fundamental knowledge than we now possess of the nature of radiation and of the atomic mechanism.

16. The Refraction of X-rays. (*a*) *Measured by Use of Bragg's Law.*—The discovery of the refraction of X-rays and the subsequent measurement of indices of refraction are excellent illustrations of the great advances which have been made in the technique of X-ray measurements since the discovery of the action of the crystal grating. One of the first observations recorded by Roentgen was that no measurable refraction of X-rays was found. Subsequent, and more precise, measurements seemed to confirm this result. For example, Barkla,[1] in a very careful investigation, failed to detect any refraction and concluded that the refractive index for wave length 0.5 Ångström differed from unity by less than 0.000006.

The first positive evidence that X-rays are measurably refracted came from the work of Stenström,[2] who showed from accurate measurements of wave length that Bragg's law of the reflection of X-rays from crystals

$$n\lambda = 2d \sin \theta$$

does not yield identical values when the wave length of a given line is computed from different orders of reflection. Hjalmer[3]

[1] *Phil. Mag.*, vol. 31, p. 257 (1916).

[2] Dissertation, LUND (1919).

[3] Quoted by SIEGBAHN, "The Spectroscopy of X-rays" (English translation), p. 22.

found, for example, that the wave length of the Fe $K\alpha_1$ line as measured in the first order by reflection from a gypsum crystal (d = 15.155 Ångströms) was 1.9341 Ångströms; while measurements in the sixth order gave 1.9306 Ångströms, nearly 0.2 per cent less.

This apparent failure of the Bragg formula was shown to be due to the refraction of the beam of X-rays as it entered the crystal, the deviation of the beam being such as to indicate *that the index of refraction is less than unity.* In Fig. 152 is shown the path of a ray as it enters the surface SS of a crystal at a glancing

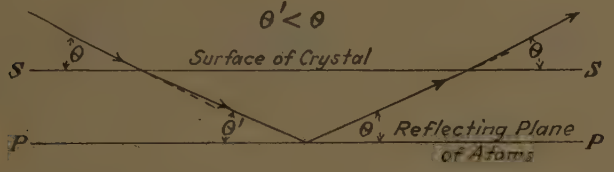


FIG. 152.—Refraction of a beam of X-rays entering the surface of a crystal, showing the reason for the apparent failure of Bragg's law.

angle θ and is incident *onto the plane of atoms PP* at an angle θ'. Bragg's law in the form

$$n\lambda' = 2d \sin \theta'$$

where λ' is the wave length *in the crystal*, gives the true law of reflection *at the crystal plane. Measurements* give θ, however, and it is λ, the wave length in *air*, that is desired. It can be shown[1] that the correct wave length λ can be obtained by the use of a slight correction factor to Bragg's equation, *viz.*,

$$n\lambda = 2d \sin \theta \left[1 - \frac{1 - \mu}{\sin^2 \theta}\right] \tag{45}$$

where μ is the index of refraction of the X-rays in the crystal. This equation contains the unknown quantities λ and μ. By making measurements in two different orders n_1 and n_2, it is possible to solve simultaneously for λ and μ. In this way, Hjalmer,[2] for example, obtained the following data for the quantity $\delta = 1 - \mu$ for gypsum:

[1] See COMPTON, A. H.: "X-rays and Electrons," p. 212.

[2] *Ann. Physik*, vol. 79, p. 550 (1926).

TABLE X.—INDEX OF REFRACTION, $\mu = 1 - \delta$, OF GYPSUM (HJALMER. *loc. cit.*)

λ, Ångströms	δ, times 10^6	$\frac{\delta}{\lambda^2}$ times 10^6
1.537	9.0	3.85
1.932	15.4	4.11
2.498	23.1	3.70
3.025	27.5	3.00
3.378	37.9	3.32
3.926	60.4	3.92
4.718	74.9	3.37
5.166	82.6	3.10

Classical theory gives for the index of refraction μ of a substance for waves of frequency[1] ν

$$\mu^2 = 1 + \frac{e^2}{\pi m} \sum \frac{n_i}{\nu_i^2 - \nu^2} \tag{46}$$

where n_i is the number of electrons per unit volume which have frequency ν_i and the summation is to be extended to all the different groups of electrons in the refracting material. If, as in X-rays, (1) the index of refraction differs from unity by only a small quantity δ, as shown by Hjalmer's results, and (2) the frequency ν of the incident radiation is very much higher than any of the frequencies ν_i of the refracting substance,[2] we may, neglecting ν_i^2 in comparison with ν^2, write equation (46) in the form

$$\mu = 1 - \frac{ne^2}{2\pi m\nu^2} \tag{47}$$

where n is the total number of electrons per unit volume. Since $\mu = 1 - \delta$, we have

$$\delta = \frac{ne^2}{2\pi m\nu^2} \tag{48}$$

or, changing ν into wave length λ,

$$\frac{\delta}{\lambda^2} = \frac{ne^2}{2\pi mc^2} = \text{a constant} \tag{49}$$

[1] See, also, equation (94), Chap. IV, which is the same formula expressed in slightly different symbols.

[2] This is true for X-rays of moderately short wave length and refracting materials of not too high atomic number.

That is, the quantity δ/λ^2 should be a constant as long as the frequency of the refracted X-rays is much greater than the frequency of any groups of electrons within the refracting substance.

The measurements of Larson[1] have shown that for mica the quantity δ/λ^2 is substantially constant over a wave-length range $1.5 < \lambda < 8.3$ Ångströms. This constancy, however, should not hold in the neighborhood of a critical frequency ν_i. Hjalmer's measurements for the index of refraction of gypsum, $CaSO_4$, given in Table X, cover a wave-length range which includes the K limit of Ca and the K limit of S. If the values of δ/λ^2, given in the table, be plotted against wave length, a graph of the type shown diagrammatically in Fig. 153 results, unique points or discontinuities apparently occurring at the wave

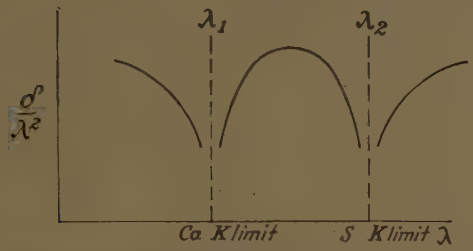


FIG. 153.—Variation of index of refraction through the K absorption limits of the atoms in a crystal.

lengths λ_1 and λ_2, which correspond approximately to the wave length of the calcium K absorption limit ($\lambda = 3.06$ Ångströms) and the sulphur K absorption limit ($\lambda = 5.01$ Ångströms).

On the basis of the classical theory, such discontinuities as are observed in Fig. 153 indicate resonance phenomena, it being assumed that there are present in the refracting medium resonating systems the natural frequencies of which correspond to the discontinuities in the curve. *These* critical frequencies shown in Fig. 153, however, correspond to the *K absorption limits* of Ca and S and *not to the frequencies which these substances radiate*, which frequencies are the K series of lines. It might be expected from classical theory that these latter frequencies should be identical with the resonating frequencies. But such is not the case. Again, a formula derived on classical theory and, in part, successful comes into conflict with experiment.

[1] *Zeit. für Physik*, vol. 35, p. 401 (1926).

(*b*) *Direct Measurement by a Prism.*—Although the index of refraction for X-rays differs only very slightly from unity, its direct measurement by a prism has been accomplished by several observers. Among the most interesting measurements are those of Davis and Slack,[1] whose method is instructive. A beam of X-rays from a target is reflected from a crystal K_1 (Fig. 154) at such an angle that a monochromatic beam, say the characteristic

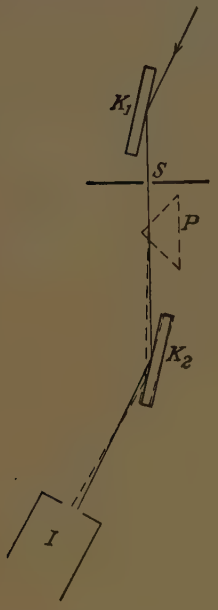


FIG. 154.—The "double" X-ray spectrometer of Davis and Slack for measuring index of refraction of X-rays by the prism method.

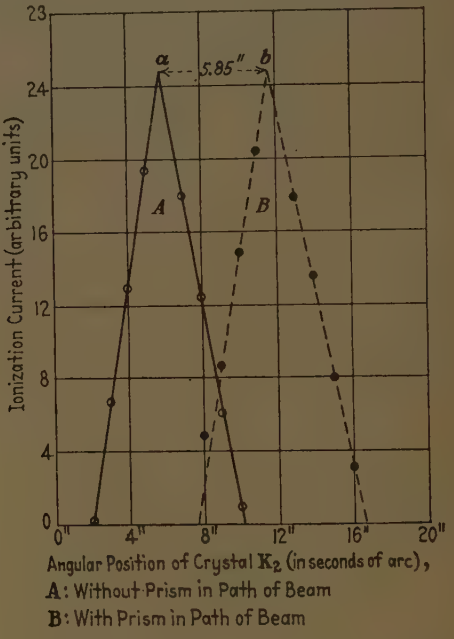


FIG. 155.—The shift in a spectral line produced by refraction through a prism (*Davis and Slack*).

$K\alpha_1$ line of the target, passes through a slit S and falls onto a second crystal K_2. When K_2 is *exactly* parallel to K_1, this beam is reflected from K_2 and enters the ionization chamber I. If K_2 be turned in either direction from *exact* parallelism, the ionization current decreases rapidly to zero, the apparent "shape" of the line, or beam, being shown as A (Fig. 155), in which the abscissæ are seconds of arc from an arbitrary zero. The point a can be located very exactly.

[1] *Phys. Rev.*, vol. 27, p. 18 (1926).

If, now, a prism P be placed in the path of the beam, as shown, the beam is deflected—in the opposite direction to that in which a beam of light is deflected, since $\mu < 1$. The angle through which the beam is deflected in its passage through the prism can be determined by observing the new position in which the crystal K_2 must be placed to reflect the beam. The shift in the position of the line A, which is the $K\alpha_1$ line of Mo ($\lambda = 0.7078$ Ångström), when a prism of aluminum with a refracting angle of 166 degrees is placed in the beam, is shown as B (Fig. 155). The angular displacement Δ between A and B is 5.85 seconds. From the ordinary law of refraction by a prism, it follows that the index of refraction, when, as in this case, Δ is very small, is

$$\mu = 1 + \sin\frac{\Delta}{2}\cot\frac{\theta}{2}$$

$$\therefore \delta = 1 - \mu = -\sin\frac{\Delta}{2}\cot\frac{\theta}{2}$$

where θ is the angle of the prism. The results obtained by Davis and Slack for a prism of aluminum for the two wave lengths $\lambda = 0.7078$ and $\lambda = 1.537$ Ångströms are as follows:

	$\lambda = 0.7078$ Å ANGSTRÖM	$\lambda = 1.537$ Å ANGSTRÖMS
Angle of prism	166 degrees	116 degrees
Mean angle of deviation	5.62 seconds	5.53 seconds
$\delta = 1 - \mu$, observed	1.68×10^{-6}	8.4×10^{-6}
δ, computed	1.77×10^{-6}	8.36×10^{-6}

The computed values of δ are obtained by use of equation (49)

$$\delta = \frac{ne^2\lambda^2}{2\pi mc^2} \tag{49'}$$

where n, the number of electrons per unit volume of aluminum, is computed from the known values of Avogadro's number N_0, the atomic weight A, atomic number Z and the density of aluminum ρ, viz:

$$n = \frac{N_0}{A}\rho Z \tag{50}$$

The computed values of δ are seen to be in excellent agreement with the observed, thus, apparently, confirming the classical theory of refraction on which equation (49) is based.

Subsequently, Davis and Slack[1] reported measurements on the index of refraction of several substances for the Mo $K\alpha_1$ line ($\lambda = 0.7078$ Ångström) as follows:

REFRACTING ELEMENT	$\delta = 1 - \mu$,
Ag.....	5.85×10^{-6}
Cu.....	5.95
S.....	1.39
Al.....	1.68
C.....	1.23

(*c*) *Measurement by Total Reflection.*—Since the index of refraction of a material for X-rays is less than unity, a beam of X-rays

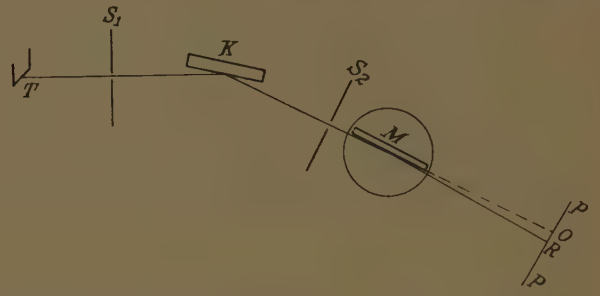


FIG. 156.—Doan's apparatus for measuring the index of refraction of X-rays by the method of total reflection.

incident onto a polished surface at a sufficiently small glancing angle should be totally reflected. One of the first measurements of X-ray refraction was by A. H. Compton,[2] using this method. The measurements of Doan[3] are instructive.

Doan's apparatus, following Compton's method, is shown schematically in Fig. 156. A beam of X-rays from a target T, after passing through a slit S_1, falls onto a crystal K, by means of which one of the characteristic lines in the spectrum of T may be reflected at a very small glancing angle onto the mirror M. With a sufficiently small angle of incidence, this beam is *totally* reflected from M and falls onto a photographic plate PP at R. M is very slowly turned during an exposure; and when the critical angle is reached, reflection ceases. This critical angle

[1] *Phys. Rev.*, vol. 27, p. 296 (1926).
[2] *Nat. Research Council, Bull.* 20, p. 50 (1922).
[3] *Phil. Mag.*, vol. 4, p. 100 (1927).

can be determined by noting the distance on the plate between the point O, which indicates the position of the direct beam, and the extreme edge of the record of the reflected beam. The metals under study were sputtered onto a highly polished optical glass surface.

The following are some of the results obtained by Doan:

TABLE XI.—INDEX OF REFRACTION OF X-RAYS BY THE METHOD OF TOTAL REFLECTION (DOAN, *loc. cit.*)

Wave length, Ångströms	Substance	Critical angle	$\delta = 1 - \mu$, times 10^6
0.7078	Ni	10′ 15″	4.42
0.7078	Ag	11′ 42″	5.76
1.389	Ni	16′ 9″	10.98
1.389	Cu	19′ 36″	16.2
1.537	Ni	24′ 40″	25.5
1.537	Cu	20′ 24″	17.7
1.537	Ag	26′ 42″	30
1.537	Au	31′ 24″	41.6

A comparison of Doan's value of δ for Ag for $\lambda = 0.7078$ Ångström with that obtained by Davis and Slack shows excellent agreement between the two methods.

Much more experimental work remains to be done before sufficient data on indices of refraction are available to serve as an adequate guide to theories of absorption, scattering, and refraction of X-rays, all three phenomena being more or less interrelated. It is very significant, however, and is suggestive of future possibilities, that experimental data on the refraction of X-rays yield, by aid of equations (49′) and (50), a value for the number of electrons per atom which is in exact agreement with that obtained by other methods, as is evidenced by the fact that the observed values of δ agree with those computed by these equations.

CHAPTER XIII

THE NUCLEUS

In Chap. X, we referred to Rutherford's experiments on the scattering of α particles and to the hypothesis of the nuclear type of atom which these experiments suggested. This was the first evidence of the existence of nuclei within atoms. The subsequent development of the Bohr atom model and its use in explaining the origin of spectral lines seemed to confirm Rutherford's hypothesis and gave some information concerning the mass of, and the charge associated with, the nucleus: Practically the entire mass of the atom is contained in the nucleus, and its charge is equal to $+Ze$, where Z is the atomic number of the atom and e is the charge on the electron. The data of spectroscopy and chemistry, however, yield no further information regarding the nucleus. Our present knowledge of the nucleus comes, in large part, from two other fields: (1) radioactivity and (2) the precision measurements of the masses of atoms by the so-called "mass spectrograph" developed by Aston in England and by Dempster in America. In this chapter, we shall give a very brief survey of these two fields, leaving it to the reader to make such further study of the literature, preferably from original sources, as the importance of the subject warrants.

Part I. The Masses of Atoms

1. Positive Rays.—Measurements of the masses of atoms are made by observing the deflection produced on positively charged ions of the substance under study by the combined action of an electric and a magnetic field, the principles of the methods used being somewhat similar to the method by which J. J. Thomson first measured the value of e/m for electrons. These positive ions in motion are frequently called *positive rays*. Two sources of positive rays are customarily employed: (1) the canal rays (see Chap. IX, Sec. 11(b)) originating near the cathode of a tube containing gas at a low pressure through which an electrical discharge is passing; and (2) the positive ions emitted

by salts when heated[1] under certain conditions. The first source is used in studying those substances which can be conveniently introduced into the discharge tube in gaseous or vapor form. The second is used when the substance is available only in the solid state.

For the early work on the deflection of positive rays by the combined action of electrostatic and magnetic fields, the student is referred to the original papers of J. J. Thomson.[2] Thomson's method is shown diagrammatically in Fig. 157. B is a large discharge tube, the cathode K of which is perforated with a very small hole through which pass the positively charged particles originating in the region immediately in front of K. These positively charged particles emerge from the opposite end of K as a narrow bundle of canal rays, the velocity of which depends

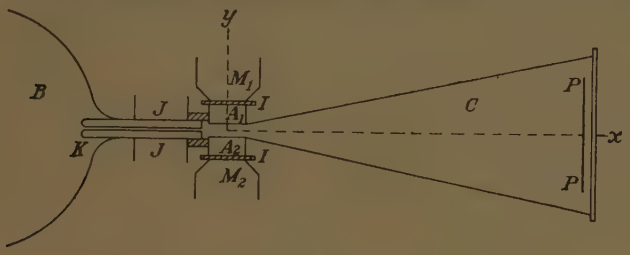


FIG. 157.—Thomson's positive-ray spectrograph.

on their charge and mass and on the potential V applied to the tube. JJ is a waterjacket for cooling the cathode. M_1 and M_2 are the poles of an electromagnet, of which A_1 and A_2 are the soft iron pole pieces electrically insulated from M_1 and M_2 by insulating strips I. A_1 and A_2 can thus be maintained at any desired potential difference, so that in the space between A_1 and A_2 we may have a magnetic field and, parallel thereto, an electric field. A positively charged particle moving from left to right in this space will experience a deflection in the plane of the paper, due to the electrostatic field, and at right angles to the plane of the paper, due to the magnetic field. After leaving the space between A_1 and A_2, the deflected particle moves in the field-free, evacuated space inside the "camera" C and falls on the

[1] See RICHARDSON: "The Emission of Electricity from Hot Bodies."

[2] *Phil. Mag.*, vol. 13, p. 561 (1907); vol. 20, p. 752 (1910); vol. 21, p. 225 (1911); vol. 24, p. 209 (1912); THOMSON, J. J.: "Positive Rays of Electricity," 2d ed. (1921).

photographic plate *PP*. Thomson found that the plate, after development, showed a series of parabola, the constants of which were dependent on the ratio E/M, where E is the charge carried by the particle (E must be, of course, an integral multiple of the charge e) and M is the mass of the particle.

Let a particle, as it enters the space A_1A_2, be moving with velocity v, initially parallel to and coincident with the x-axis of a system of rectangular coordinates with origin in the space A_1A_2. Let the mass of the particle be M and its charge E. Also, let Y and β be, respectively, the electrostatic and the magnetic fields, and S the length of the path through the fields, it being assumed that the fields are constant over the length S and that they terminate sharply. As a result of the passage through the field, the particle will experience a deflection y' (from the x-axis), due to the electric field, given by

$$y' = \frac{1}{2}\frac{YE}{M}\left(\frac{S}{v}\right)^2 \tag{1a}$$

and a similar deflection z' in the z direction due to the magnetic field, assuming that the deflection is small compared to the radius of the circular path, given by

$$z' = \frac{1}{2}\frac{\beta E}{Mv}S^2 \tag{1b}$$

After leaving the fields, the particle moves in a straight line. If the distance of the photographic plate *PP* from the space A_1A_2 is large compared to the length of the path S, the point where the particle strikes the plate will have coordinates y and z which are, respectively, proportional to y' and z'. It follows readily that a relation between y and z is given by (eliminating v from equations (1))

$$z^2 = C\frac{E}{M}\frac{\beta^2}{Y}y \tag{2}$$

where C is a constant depending on the dimensions of the apparatus. This is the equation of a parabola. Accordingly, particles having various velocities v as they enter the field space A_1A_2, but having the same ratio E/M, should make a parabolic trace on the plate, as Thomson found. For the same value of the fields β and Y, particles with a *different* ratio of E/M should produce on the plate another parabola. The fact that these

traces found by Thomson were reasonably sharp indicated that atoms of a given kind all have the same mass.

By a systematic study of the relative positions of the various parabolic traces appearing on a series of plates, Thomson was able to determine the origin of the traces. Traces due to H^+, H_2^+, O^+, O_2^+, CO^+, etc., were identified. Knowing the masses of these "standards," the masses of atoms producing other traces could be determined. Thomson found that when neon, atomic weight 20.2, was introduced into the discharge tube, instead of a *single* trace, there were *two* traces corresponding to atomic weights 20.0 and 22.0 and suggesting that there are two kinds of neon atoms, one having atomic weight 20.0 and the other having atomic weight 22.0. A direct method was thus available for measuring the masses of atoms. This method was substantially modified and rendered more precise by Aston, whose "mass spectrograph" has very greatly extended our knowledge of atoms.

2. Isotopes. (*a*) *Aston's "Mass Spectrograph."*—Astons' improvements[1] in the methods of positive-ray analysis consist

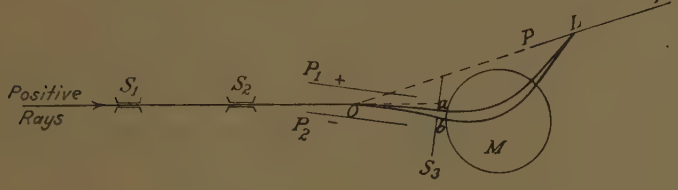


FIG. 158.—Schematic arrangement of Aston's "mass spectrograph."

(1) in securing greater dispersion and (2) in bringing all ions with a given ratio E/M to a *focus* (instead of spreading them out into a parabola), thereby securing greater sensitivity. The principle employed by Aston is represented in Fig. 158. The positive rays from a discharge tube (not shown) pass through a narrow slit S_1 in the anode, thence through a second slit S_2, from which they emerge into the space between the metal plates P_1 and P_2 between which can be maintained an electric field of any desired intensity. This field causes a deflection of the particles toward P_2, the amount of the deflection being greater the less the velocity of the particles. Since the positive-ray stream

[1] Aston's papers are found in the *Phil. Mag.*, vols. 38 to 49 (1919 to 1925); see also *Nature*, vol. 116, p. 208 (1925) and vol. 117, p. 893 (1926). ASTON'S "Isotopes," 2d. ed. (1924), also gives an account of the subject.

contains a wide range of velocities, the stream will be broadened as it passes through the field, the more swiftly moving ions passing through the wide slit S_3 on the side *a* and the more slowly moving ones passing on the side *b*. After leaving S_3, this diverging stream of ions enters a magnetic field at right angles to the plane of the paper, maintained between the circular pole pieces *M* of an electromagnet. This magnetic field causes deflections, as shown, the more slowly moving ions being deflected more than the faster ones, the result being that when the ions emerge from the magnetic field they are moving in *converging* directions in such a way that they are brought to a "focus" at some point *L*. It turns out that, with suitable design of the apparatus, the locus of point *L* for ions having various ratios of E/M is nearly a straight line passing through point *O*. Consequently, a photographic plate placed in position *PP* will record a number of "lines," each line corresponding to a particular ratio E/M. In part, from the known dimensions of the apparatus and, in part, by introducing into the discharge tube certain known substances —H_2, O_2, CO, CO_2, etc.—as calibrating standards, the masses of other ions can be determined.

The lines produced by such ions as O^+, O_2^+, CO^+, N_2^+, CO_2^+, which are made up of atoms the atomic weights of which are, as measured, exact integers (*e.g.*, 16.00 for oxygen; 12.00 for carbon; etc.) are, in each case, *single* lines, indicating that the atoms of each of these substances all have the same mass. When, however, neon, the atomic weight of which, namely, 20.2, departs measurably from an integer, is introduced into the tube, *no line corresponding to the mass* 20.2 *is found*, but, instead, there are *two* lines, the one, stronger, corresponding to a mass of 20.0, and the other, weaker, to a mass of 22.0. Unmistakably, there are, as Thomson showed, two kinds of neon atoms which differ from each other only in having *different* masses, *which masses are integers* when the mass of the oxygen atom is taken as 16.00.

Similarly, when chlorine is introduced into the tube, no line is observed which corresponds to the chemically determined weight of chlorine, namely, 35.46, but, instead, there are *two* lines corresponding to the *integer* values 35.0 and 37.0, the former being the more intense line. There are, thus, two kinds of chlorine atoms differing from each other in atomic weight but being *identical as regards all their other chemical and physical properties.* Hence, they are called *isotopes.* Chlorine is, thus, a mixture of two kinds

of atoms, of respective masses 35.0 and 37.0 in such proportion that the average mass per atom of a large number of atoms—which is the mass given by chemical determinations—is 35.46.

(*b*) *Dempster's Method.*—Dempster's method of measuring the masses of atoms differs from Aston's in that (1) the photographic plate is replaced by an electrical method of measurement and (2) the disposition of the electric and magnetic fields is materially different. Dempster's apparatus[1] is shown schematically in Fig. 159. An electrically heated metal cylinder A, which serves as anode, has on its front surface f a salt of the element under study. This heated salt is bombarded by electrons from the hot wire ww, which is heated by the battery B_1, the wire being main-

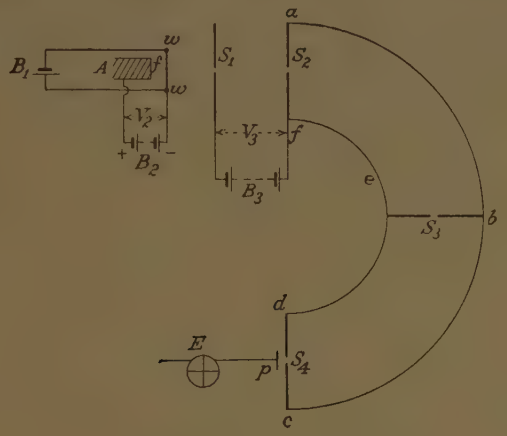


FIG. 159.—Dempster's "mass spectrograph."

tained at a potential difference V_2 of -30 to -60 volts with respect to A by means of the battery B_2. Dempster found that, when so bombarded, the anode emitted positively charged ions. These ions, after passing through the slit S_1, are accelerated toward the slit S_2 by means of the potential difference V_3 of some 800 to 1,000 volts. On emerging from the slit S_2, the ions enter the space *abcdef* in which is maintained a uniform magnetic field, perpendicular to the plane of the paper, by means of which the ions are caused to move in a circular path toward the slit S_3, the radius r of the circle being determined by the velocity v of the ions as they enter S_2, their mass M, and charge E, as well as the

[1] For Dempster's articles, see *Phys. Rev.*, vol. 11, p. 316 (1918); vol. 18, p. 415 (1921); and vol. 20, p. 631 (1922).

intensity of the magnetic field H, according to the well-known equation

$$HEv = \frac{Mv^2}{r}$$

When the ions move in circles defined by the *three* slits S_2, S_3, and S_4, they pass through S_4 and fall upon the metal plate p, which thus acquires a positive charge at a rate which can be determined by the electrometer E. (Dempster used a sensitive electroscope.) For a given ratio of E/M and field H, the value of r

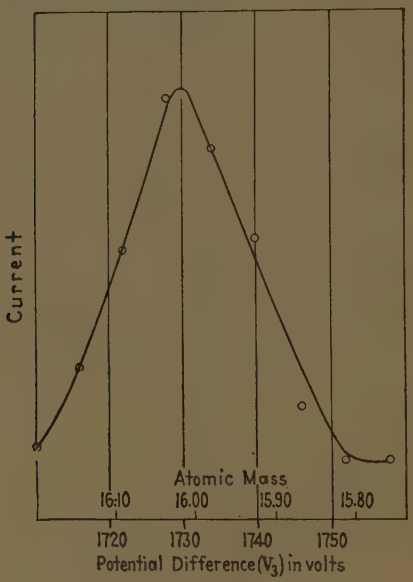


FIG. 160.—The oxygen (O^+) line with Dempster's apparatus.

and, therefore, of the current I registered by the electrometer depends on the potential difference V_3. A curve plotted between I and V_3 shows sharp maxima, each of which corresponds to a definite value of E/M. In part, from the known constants of the apparatus and, in part, by use of known ions, Dempster was able to identify these maxima with definite ions. A sample of the data for the ion O^+ is shown in Table I. Figure 160 shows graphically the relation between V_3 and I. Column three of Table I gives the computed value of M (in terms of O = 16). Of course, the finite width of the graph is due to the necessity of employing finite slit widths, since all the ions entering the slit S_4

TABLE I.—DEMPSTER'S DATA FOR THE ION O^+

V_3 (volts)	I	M (computed)
1,758	7.3	15.76
1,752	7.3	15.81
1,746	15.6	15.87
1,740	38.6	15.92
1,734	51	15.98
1,728	58	16.03
1,722	37	16.09
1,716	21	16.14
1,710	10	16.20

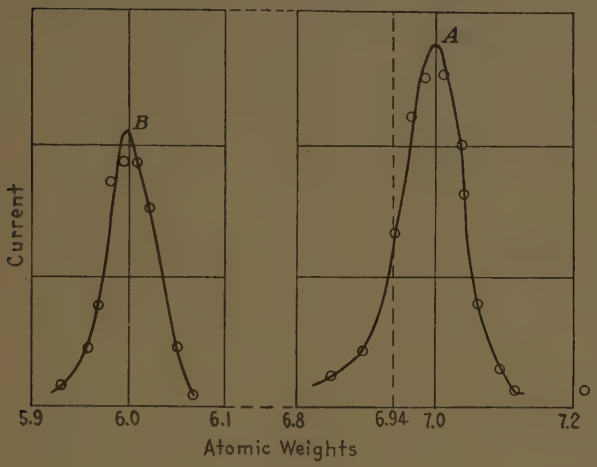


FIG. 161.—The isotopes of lithium, as measured by Dempster.

in this experiment were O^+ ions. The *maximum* of the curve corresponds to the weight of the oxygen atom.

When employing a salt containing lithium, Dempster found two maxima in the neighborhood of the atomic weight of lithium, 6.94, as shown in Fig. 161, in which the abscissæ are the values of M, the computed mass of the ion, as determined semiempirically from the constants of the apparatus. The one maximum A corresponds within the limits of error of measurement to atomic weight 7.00; the maximum B corresponds to 6.00. There is no indication of atoms of lithium with weight 6.94, the chemically determined atomic weight of lithium, which is indicated in Fig. 161 by the dotted line. Dempster, by this method, has analyzed

a number of elements—magnesium, lithium, calcium, and zinc—and has found them to be made up of isotopes, the masses of which are, within the limits of error of measurement, integers in terms of the mass of the oxygen atom as 16.

(*c*) *Isotopes of the Elements.*—With few exceptions, practically all of the more important elements have now been studied, and many of them have been found to consist of mixtures of atoms, *i.e.*, isotopes, which have very nearly integer atomic masses. The isotopes for the various elements are shown in Appendix I(*b*), in connection with the periodic table of the elements. Some of the elements, for example mercury, are observed to be a mixture of many different kinds of atoms, all having practically integer masses. We thus return to Prout's hypothesis and, now on the basis of unambiguous *experimental evidence*, assert that *the masses of all atoms are integer multiples of a unit mass which is one-sixteenth of the mass of the oxygen atom.* The presumption is inescapable that this unit mass must be a definite physical entity and must be the primordial substance out of which all atoms are built. The two kinds of lithium atoms, which have masses of 7.00 and 6.00, must contain, respectively, 7 and 6 of these units; the two kinds of chlorine atoms contain, respectively, 35 and 37 of these units; and so on.

What is this unit? We may *guess* that it is the nucleus of the hydrogen atom, the mass of which is very nearly, *but not quite*, unity, namely, 1.0078, and which has a charge $+e$. This particle is called the "proton." If this surmise be correct, the helium nucleus should contain 4 protons and should have a mass of 4.0312 and a charge of $+4e$. The helium nucleus, however, *i.e.*, the α particle, *actually* has a mass of 4.00 and a charge of $+2e$. We can explain these facts by assuming that (1) the α particle is made up of 4 protons (total charge $+4e$) and 2 electrons (total charge $-2e$), giving to the α particle a *net* charge of $+2e$; and (2) when these 4 protons and 2 electrons combine to form an α particle, there is a loss of mass of 0.0312 gram, which is transferred into radiant energy, perhaps by a kind of superchemical reaction. According to the theory of relativity, there is a definite equivalence between radiation and matter, such that a definite mass of matter m is equivalent to a quantity of radiation E, according to the relation

$$E = mc^2$$

where c is the velocity of light. For every 4 grams of helium formed in this way from hydrogen, there should be a loss of mass of 0.0312 gram and a consequent emission of radiant energy E equal to

$$E = 0.0312 \times (3 \times 10^{10})^2 \text{ ergs}$$

—an amount of energy sufficient to raise the temperature of some 200 tons of water from 0 to 100°C.! Clearly, this is a cosmical, and not a terrestrial, process.

Once the α particle is formed, it appears to be an exceedingly stable structure, since there is no evidence of any kind indicating the breaking up of these particles. They can serve as units, perhaps in connection with protons, in building up the nuclei of the heavier elements. The oxygen nucleus, for example, should on this hypothesis consist of 4 α particles, while the nitrogen nucleus, which has atomic mass 14, cannot be made up entirely of α particles but might contain 3 α particles, 2 protons, and 1 additional electron to give it a mass of 14 and a net charge of $+7e$.

This surmise is, in part at least, confirmed by the remarkable experiments of Rutherford, in which the atoms of the lighter elements are bombarded by the swiftly moving α particles ejected from radioactive materials. In these experiments Rutherford has obtained unmistakable evidence of the disruption of the atomic nuclei, and he finds that *protons* can be "knocked out" of *nitrogen* atoms but not out of oxygen atoms. For an account of these experiments, the reader is referred to the original articles.[1]

(*d*) *The Separation of the Isotopes.*—There have been numerous attempts to separate the isotopes of the elements in appreciable quantities, but these attempts have met with only partial success. The usual methods of separating elements from each other are based upon *differences* in *chemical* and *physical* properties. As we have seen in previous chapters, the properties of a given atom are determined by the number and arrangement of the extranuclear electrons. The isotopes of a given element, however, are *identical* both as to the number and arrangement of these electrons.

[1] RUTHERFORD: *Phil. Mag.*, vol. 37, p. 537 (1919) and vol. 41, p. 307 (1921); *Nature*, vol. 109, p. 614 (1922); RUTHERFORD and CHADWICK: *Phil. Mag.*, vol. 42, p. 809 (1921); vol. 44, p. 417 (1922); vol. 48, p. 509 (1924). Many other articles dealing with this important subject will be found.

The two kinds of lithium atoms have 3 extranuclear electrons each. They have, therefore, identical chemical properties; identical[1] spectra; and are quite indistinguishable from each other except for those properties which depend only on mass. We may picture the Li(6) nucleus as containing 1 α particle, 2 protons, and 1 electron; and the Li(7) nucleus as containing 1 α particle, 3 protons, and 2 electrons. In either case, the atomic number, *i.e.*, the *net* positive charge on the nucleus, is 3. Incidentally, since the average mass of the lithium atom is 6.94, we conclude that Li(7) is much more abundant than Li(6), which probably means that the nuclear structure of Li(7) is more stable than that of Li(6).

The methods of separating isotopes, therefore, can be based only on such differences in behavior as result from differences in mass. The mass spectrograph does actually separate isotopes of the elements. By replacing the photographic plate *PP* in Aston's apparatus (Fig. 158) by suitably disposed slits, we should be able to collect one kind of neon atoms, say, in one compartment and the other kind in another. This method has actually been tried but the number of atoms obtainable by this method is so exceedingly minute that it is almost impossible to get a quantity of any isotope sufficient for any test, physical or chemical.

A method based on differences in rates of evaporation as a result of different atomic masses has been somewhat more successful. In mercury, for example, which has several isotopes, the lighter constituents should evaporate from the surface of (liquid) mercury at a slightly greater rate than the heavier constituents. Bronsted and Hevesy[2] allowed mercury vapor evaporating from the liquid maintained at a temperature of some 50°C. to condense onto a surface cooled by liquid air. After several "fractionations" they prepared from nearly 3 litres of mercury two portions of about 0.2 cc. each which differed from each other in density by a few hundredths of 1 per cent—

[1] There is, however, distinct evidence showing that different isotopes of a given element emit slightly different *band* spectra; also minute differences in the frequencies of line spectra have been observed due to difference of mass of the nuclei in somewhat the same way as the greater mass of the helium nucleus results in a larger value of the Rydberg constant for that element than for hydrogen. See "Molecular Spectra in Gases," *Nat. Research Council Bull.* 57, Chap. V.

[2] *Nature*, vol. 106, p. 144 (1920); vol. 107, p. 619 (1921). *Phil. Mag.*, vol. 43, p. 31 (1922).

not a complete separation, but sufficient to serve as a confirmatory check on the conclusions from the mass spectrograph.

3. The Packing Effect.—The data obtained by the use of the mass spectrograph indicates, beyond question, that the nuclei of atoms are built up of certain units, which units are probably protons and electrons. We saw however, that in order to explain the fact that the mass of the helium atom is not quite four times the mass of the hydrogen atom, it was necessary to assume that the "packing" of 4 protons and 2 electrons together to form the helium nucleus results in a loss of mass. This loss of mass in the formation of nuclei from protons and electrons is called the *packing effect*. There is every reason to believe that the packing effect should play a part in the formation of all nuclei, although the circumstance that the masses of all atoms heavier than helium are whole numbers, according to the above mentioned measurements of Aston and of Dempster, indicates that in the grouping together of alpha particles to make nuclei the packing effect must be small. For example, the mass of the oxygen atom is almost exactly four times the mass of the helium atom. When 4 α particles unite to form an oxygen nucleus, the loss of mass is proportionately very much less than in the formation of a helium nucleus from protons. In the case of the Li(7) atom, which, presumably, contains 1 alpha particle and 3 protons—the mass of the electrons is negligible—the mass should be slightly more than 7.00, namely, 7.023, if the 3 protons are *not* subjected to the packing effect. The difference between 7.00 and 7.023 is *almost* within the limits of experimental error. The study of the packing effect in atoms of higher atomic number than helium demands more precise data on atomic masses.

Aston has attacked this problem and has evolved an improved mass spectrograph,[1] which has a resolving power[2] of 1 part in 600 and a precision in the determination of mass in terms of the mass of the oxygen atom as 16.000, of 1 part in 10,000. This remarkable achievement has resulted in the discovery of several new isotopes, and in the determination of masses with a precision heretofore unknown. Some of these new measurements by Aston are given in Table II. Column three of this table shows the

[1] ASTON, F. W.: The Bakerian Lecture, *Proc. Roy. Soc.* (London), vol. 115, p. 487 (August, 1927).

[2] That is, two atoms whose masses differ by only 1 part in 600 are shown as separate "lines."

"mass number" of the several atoms, *i.e.*, the number which gives the number of *protons* in the nucleus. We thus have associated with each atom *three* fundamental quantities—*atomic number*, *mass number*, and *mass*. To these may be added a fourth—the chemically determined *atomic weight*, or, more correctly, the *combining weight*. For chlorine, for example, these four quantities are as follows:

Atomic number	17
Mass numbers	35 and 37
Masses	34.983 and 36.980
Combining weight	35.458

It is observed from Table II that, except in the case of oxygen, which is taken as a standard, and also of fluorine, the *masses* of atoms are *not* whole numbers but differ from whole numbers by very small amounts. These precise measurements give for each

TABLE II.—THE MASSES OF ATOMS BY ASTON'S PRECISION MASS SPECTOGRAPH

Element	Atomic number	Mass number	Packing fraction, times 10^4	Atomic masses
H	1	1	77.8	1.00778
He	2	4	5.4	4.00216
Li(6)	3	6	20	6.012
Li(7)	3	7	17	7.012
Bo(10)	5	10	13.5	10.0135
Bo(11)	5	11	10.0	11.0110
C	6	12	3.0	12.0036
N	7	14	5.7	14.008
O	8	16	(standard)	16.000
F	9	19	0.0	19.000
Ne(20)	10	20	0.2	20.0004
Ne(22)	10	22	2.2(?)	22.0048
P	15	31	−5.6	30.9825
Cl(35)	17	35	−4.8	34.983
Cl(37)	17	37	−5.0	36.980
Ar(36)	18	36	−6.6	35.976
Ar(40)	18	40	−7.2	39.971
As	33	75	−8.8	74.934
Br(79)	35	79	−9.0	78.929
Br(81)	35	81	−8.6	80.926
Xe(134)	54	134	−5.3	133.929
Hg(200)	80	200	+0.8	200.016

of the atoms measured the *packing fraction*—as Aston calls it—which is "the gain or loss of mass per proton when the nuclear packing is changed from oxygen to that of the atom in question." The packing fractions for the several elements are given in column four of Table II. The packing fraction of carbon is +0.0003, and its mass is 12.0036. Aston finds that starting with hydrogen, the packing fraction decreases rapidly with succeeding elements, reaches a minimum of −0.0009 in the neighborhood of elements of atomic number 30 to 40, and then *increases* again, becoming +0.00008 for mercury. High packing fractions (taking O = 16.000 as standard) indicate looseness of packing or comparative instability of the nucleus. This increase in the packing fraction toward the end of the periodic table of the elements may perhaps foreshadow the nuclear instability which is the cause of radioactivity. At any rate, these precise determinations of the masses of atoms offer, perhaps, a new line of attack on the problem of nuclear structure.

PART II. RADIOACTIVITY

The mass spectrograph yields precise data concerning the *masses* of the nuclei of atoms but gives no *direct* clue to the *structure* of the nucleus. From the circumstantial evidence that the masses of all the atoms are very nearly whole numbers, we *infer* that atomic nuclei are built up of fundamental units of some kind, which units we may assume are the so-called "protons." For direct evidence, meager though it is at present, we turn to the field of radioactivity.

4. Becquerel's Discovery.—The discovery of the phenomenon of radioactivity, although quite accidental, resulted directly from the discovery of X-rays. Roentgen had showed that X-rays are emitted by those parts of the discharge tube which are bombarded by the cathode rays. This bombardment was also accompanied by the emission of the well-known greenish or bluish fluorescence. The question arose: Is fluorescence always accompanied by the emission of X-rays?

Several investigators had apparently found that fluorescent bodies activated by sunlight gave out a type of radiation which, like X-rays, was able to pass through black paper and to affect a photographic plate. In February, 1896, a few months after the discovery of X-rays, Henri Becquerel[1] was trying an experiment

[1] BECQUEREL'S papers appear in *Compt. rend.*, vol. 122 (1896).

of this kind using as the fluorescing substance the double sulphate of uranium and potassium. After preparing the experiment and while waiting several days on account of inclement weather for sunshine, Becquerel discovered that the specimen even in the dark emitted a radiation which penetrated the black paper, thin sheets of metal, and other substances opaque to ordinary light and that exposure of the fluorescing substance to sunlight had no effect on the phenomenon.

Becquerel soon found that this radiation was emitted by uranium irrespective of its state of chemical combination and that there was no connection whatever between this phenomenon and phosphorescence. Further, the phenomenon was found to be quite independent of the temperature of the uranium compound. It was later discovered that these rays from uranium possess the power of discharging electroscopes by rendering the air through which they pass conducting.

This property of "radioactivity," as it was called, was found to be possessed by several substances. Among these substances were thorium and two new elements—polonium and radium—discovered by M. and Mme. Curie, the latter substance being more than a million times more active than uranium.

5. The Types of Radioactive Radiations.—(*a*) Like X-rays, the rays from radioactive materials affect a photographic plate, cause fluorescence, and ionize gases through which they pass. Unlike X-rays, the radioactive rays are of three types, known, respectively, as the α-rays, the β-rays, and the γ-rays. There are various ways of showing the existence of these various kinds of rays. Schematically, if a small quantity of radium preparation be placed at the bottom of a small hole drilled into a heavy metal block B, the emerging rays can be, ideally, divided into the three groups by use of a magnetic field of suitable strength at right angles to the plane of the paper and directed away from the reader, as is shown in Fig. 162. One group is bent into a circular path to the right and will cause an impression on a photographic

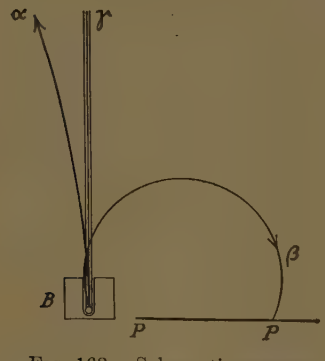


FIG. 162.—Schematic representation of the three types of rays from radioactive materials.

plate *PP*. These are the β-rays. From the direction of their deflection, it follows that they must be negatively charged particles. By studying quantitatively their deflection in magnetic and electric fields, it was shown that these particles are electrons which are ejected from radioactive materials with, in some cases, very high velocities, there being, in general, different groups with different velocities from any one material. A second type of radiation is deflected by *strong* fields toward the left. This type consists of positively charged particles called "α particles," which were shown to possess a ratio e/m much smaller than that for the β-rays; in fact, a ratio of the order of magnitude of that for *atoms*. These α particles were found to have a mass 4 (taking the mass of the oxygen atom as 16) and to carry a charge $+2e$. This identified them with the nuclei of helium atoms. The third type of radiation, the γ-rays, proceeds undeviated by either electric or magnetic fields, has a very high penetrating power, and is now known to consist of electromagnetic radiations of very short wave length lying, in general, in the spectral region beyond the shortest X-rays.

These three types of rays are further differentiated from each other by their penetrating power. The α-rays are absorbed by a few cemtimeters of air at ordinary pressure. They are reduced in intensity one-half by passing through 0.005 mm. of aluminum. Their initial velocities are of the order of 2×10^9 cm.-sec^{-1}. The β-rays are, roughly, one hundred times more penetrating, since it requires something like 0.5 mm. of aluminum to reduce their intensity to half. The initial velocities of the β-rays, in some instances, exceed 99 per cent of the velocity of light. The γ-rays are able to penetrate many centimeters of even so dense a metal as lead.

(*b*) The technique which has been developed for studying, classifying, and interpreting the phenomena of radioactivity constitutes almost a separate science by itself. For details, the reader is referred to special treatises[1] and to the original articles. As an illustration, we shall describe briefly the methods used by Rutherford and his collaborators in determining the properties of, and in identifying, the α particles.

[1] RUTHERFORD: "Radioactive Substances and Their Radiations" (1913); SODDY: "The Chemistry of the Radio Elements" (1914); HEVESY and PANETH: "Radioactivity," translated by R. W. Lawson (1926); KOVARIK and MCKEEHAN: "Radioactivity," *Nat. Research Council, Bull.* No. 51 (1925).

First, by studying the deflections produced by electric and magnetic fields Rutherford determined the ratio E/M where E is the charge carried by the α particle and M is its mass. His apparatus for this purpose is shown, schematically, in Fig. 163. A fine wire W coated with an active deposit of radium C, which emits α particles, was placed in a groove in a block B within a highly evacuated vessel which was in a *very strong* magnetic field perpendicular to the plane of the figure. The α particles emitted by W move with velocity v in circular paths and some of them pass through the slit S and fall upon the photographic

FIG. 163.—Rutherford's apparatus for measuring the magnetic deflection of α rays.

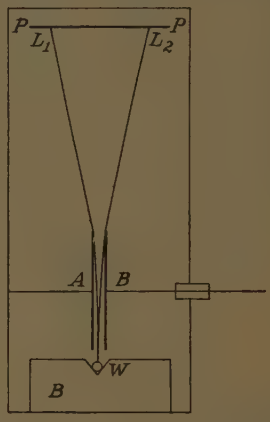


FIG. 164.—Rutherford's apparatus for measuring the electrostatic deflection of α rays.

plate PP at L_1 with the magnetic field directed away from the reader, and at L_2 with the field reversed. The two traces L_1 and L_2 were sharp, so that the radius r of the circular path could be quite accurately determined. This gave, since the field H was known,

$$Hr = \frac{M}{E} v.$$

To determine v it was necessary to measure the deflection produced by an electrostatic field. This proved to be difficult because of the very small deflections. The wire W and block B (Fig. 164) were arranged as in the previous experiment. Immediately over the wire were two metal plates A and B some 5 cm. long and 0.2 mm. apart, between which could be maintained an electric field of the order of 20,000 volts per centimeter. The α

particles, in passing through this field, are deflected at right angles to their path and by reversing the field two "lines" L_1 and L_2 were produced on the photographic plate PP. From the distance between these lines and the dimensions of the apparatus, it was possible to determine the deflection produced by the electrostatic field and thus to get a numerical value of the quantity $\frac{M}{E}v^2$. (The method used in getting this expression is somewhat similar to that used in getting equation (1a).) By combining these two experiments both E/M and v could be determined. Rutherford found that, for the α particles from radium C, $v = 2.06 \times 10^9$ cm. per second and $E/M = 5{,}070$ e.m.u. per gram.

The value of E/M for the hydrogen atom is (see Chap. VI, Sec. 4) about double this, namely, 9,650. As in the case of the electron, to determine M it became necessary to measure E. A known quantity of radium C was deposited on a plate P (Fig. 165) placed in a highly evacuated vessel. The α particles, after passing through a window W of known area and covered with very thin aluminum, fell upon the metal plate C, giving thereto the charge which they carry. This charge acquired by the plate in a known time was measured by an electrometer. To obtain the charge per particle it was necessary to know the number of particles.

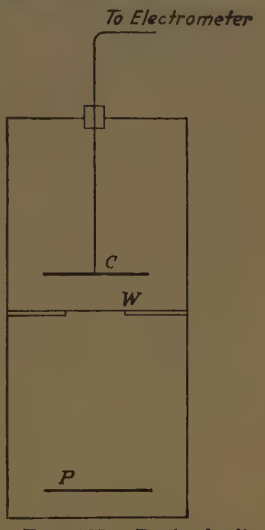


FIG. 165.—Rutherford's apparatus for measuring the charge carried by the α-rays from a known quantity of radioactive material.

Rutherford and Geiger measured ("counted") by means of the apparatus shown in Fig. 166, the number of α particles emitted per second by a known quantity of radium C. A known quantity of radium C was deposited on a disk D which was placed inside the highly evacuated vessel A at a known distance from a small circular opening S of known area which was covered by a sheet of mica thin enough to allow the passage of the α particles into a brass chamber C. This chamber was evacuated to a pressure of several millimeters of mercury and had at its center an insulated wire WW which, by means of a battery B, was maintained at a potential, with respect to the

walls of the cylinder, just less than the critical discharge potential. When an α particle entered C through the aperture S the ionization caused by the passage of the particle lowered the critical potential by an amount sufficient to allow the passage through the cylinder of a momentary current, which could be detected by a "kick" in the electrometer E. In this way, Rutherford and Geiger were able to detect the passage of *single* α particles. The quantity of radium on D, the distance DS, and the area of S were so adjusted that several particles per second entered the chamber C. Thus, knowing the rate at which the α particles passed through S, the aperture which S subtended at D, and the quantity of radium on D, it was possible to determine the total number of α particles emitted per second per gram of radium.

The total number of particles emitted per second by the radium preparation in the experiment illustrated in Fig. 165

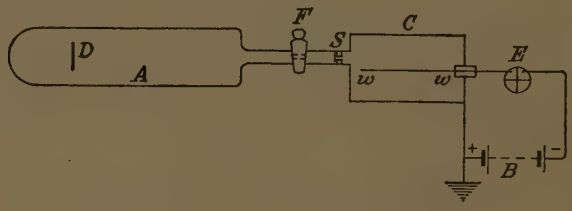


FIG. 166.—Apparatus of Rutherford and Geiger for "counting" α particles.

could thus be computed and thence the charge per particle. It was found that each α particle carried a charge of about 9.3×10^{-10} e.s.u.—approximately twice the value 4.77×10^{-10} of the charge per electron. From this it follows that the α particle has (1) a charge $+2e$ and (2) from the previously determined value of E/M, a mass approximately four times the mass of the hydrogen atom. In other words, the α particle is a helium atom with a double charge.

This conclusion regarding the nature of the α particles was confirmed, both qualitatively and quantitatively, by the observation that *helium* is produced as a result of radioactive disintegration. Rutherford showed, from the measurements on counting α particles, that 1 gram of radium in *radioactive* equilibrium with its surroundings should emit 1.3×10^{10} α particles per second. If the α particle is a (charged) helium atom 1 gram of radium should, in 1 year, emit about 0.160 cc. of helium. A direct

laboratory study of the rate of emission of helium from radioactive materials, as well as a study of the evolution of helium from radioactive minerals, gave results in satisfactory quantitative agreement with the quantity predicted from the rate of α-particle emission.

The evidence is quite complete, therefore, that the α particles are helium atoms with a charge $+2e$. Since the neutral helium atom has 2 (extranuclear) electrons, the conclusion is obvious, therefore, that the α particles are helium *nuclei*.

6. Origin of the Rays.—From the fact that the α-rays have atomic mass 4, one concludes, at once, that they must come from the nuclei of atoms, since in our present concept of atomic structure there is no place in the extranuclear region of an atom for particles of mass so large as that of the α particle. And it follows at once, that a radioactive atom which has lost an α particle has thereby decreased in atomic weight by 4 units—it must, therefore, be a different type of atom. The α particles emitted by a given radioactive element all have the same velocity, from which we conclude that each α particle is expelled as a result of a *definite atomic process*—a *disintegration*. That each disintegrating atom gives out 1 α particle was shown by actually counting the number of α particles given out by a known amount of a radioactive substance in a given time and comparing the number so obtained with the known rate of disintegration of the material.

The origin of the β-rays cannot be so definitely fixed, partly because we know that the atom possesses electrons in its extranuclear structure, partly because the β-ray emission from a given radioactive element consists, in general, of β particles having a wide range of velocity. The most swiftly moving have a velocity which approaches, within a small fraction, the velocity of light. Others have much smaller velocities. The magnetic spectrum of the β-rays from some of the radioactive elements shows sharp lines, indicating groups of β particles with definite velocities. And it is probable that some of them come from the nucleus; others, by a kind of secondary photoelectric process, from the extranuclear structure.

The γ-rays have been studied, in part, by reflection from a crystal grating, as in the case of X-rays and, in part, by a secondary photoelectric method in which the velocities of the photoelectrons liberated by γ-rays was measured by the mag-

netic spectrograph, and from these velocities the frequencies of the exciting radiation could be computed. In this way, it is found that the γ-rays cover a wave-length range extending from about $\lambda = 0.005$ Ångström to beyond $\lambda = 1.0$ Ångström. The rays of shorter wave length in this region must certainly come from the nucleus, for we can fix definitely the shortest rays which the extranuclear structure of any atom can radiate. This is the $K\gamma$ line of uranium which has a wave length of 0.1085 Ångström. Any line radiation of *shorter* wave length must come from the nucleus.

Primarily, then, the phenomena of radioactivity have their origin in *nuclear* processes, although, as secondary effects, the extranuclear structure is involved.

7. The Radioactive Disintegration Series.—A systematic study of the radioactive process and of disintegration products has led to the generalization that there are several series of the radioactive elements, the elements of a given series being so arranged that each is a disintegration product of a preceeding element. Thus, the uranium atom when it disintegrates emits an α particle, mass 4, and charge $+2e$. Uranium has an atomic mass of 238 and a (net) nuclear charge of $+92e$. After emitting the α particle the remaining nucleus must have mass 234 and a charge $+90e$. This is an element of atomic number 90. It is called "uranium X_1" (UX_1). Although possessing atomic number 90, UX_1 cannot be thorium, for which also $Z = 90$, since thorium has atomic mass 232.

The UX_1 atom, in disintegrating, emits a β particle, charge $-e$, from its nucleus. The effect of this is to *increase* the *net* nuclear positive charge to $+91$ and therefore, also, the atomic number to 91 but to leave the *mass* unchanged. This new element is called UX_2. It, in turn, emits a β particle. The resulting product, uranium II, (U II) has atomic number 92, and an atomic mass of 234. It is, therefore, an *isotope* of uranium.

U II emits an α particle, producing ionium, mass 230, atomic number 90. Ionium is, therefore, an isotope of UX_1. Ionium, in turn, emits an α particle and becomes *radium*, atomic mass 226, atomic number 88. A direct determination of the atomic weight of radium by chemical methods yields 226. Radium, then, is a disintegration product from uranium. Continuing in this way radium G is finally reached which has an atomic mass of 206 and an atomic number of 82. Radium G is there-

fore an isotope of *lead*. Radium *G* is not radioactive and is, therefore, the end of the series.

Another series of disintegrations starts with thorium, atomic number 90 and atomic mass 232, and ends with an element of atomic number 82 and atomic weight 208. This is also an isotope of lead. These two series are shown by the conventional diagram of Fig. 167. The elements in the same vertical rows are isotopes;

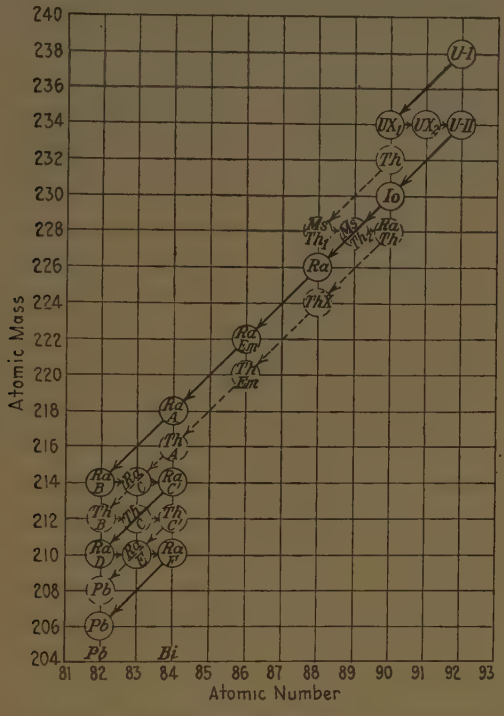


FIG. 167.—The radioactive disintegration series of uranium and thorium.

while the elements in the same horizontal rows are isobars, *i.e.*, elements which have the *same* atomic mass but *different* chemical properties, since they have different atomic numbers and therefore different extranuclear electron structures.

The end products of these two series are isotopes of lead with atomic masses 206 and 208, respectively. Ordinary lead has atomic weight 207.2. The atomic weight of lead, however, depends somewhat on the source. Uranium-bearing minerals usually contain lead—a fact in itself confirming the series of radioactive transformations from uranium to lead. The same is true of certain thorium-bearing minerals. Further, the atomic

weight of lead coming from uranium-bearing minerals is only a little over 206, while lead associated with Norway thorite has an atomic weight of 207.9, which is nearly the value 208 predicted for the end products of the thorium series.

These radioactive transformation series, therefore, from uranium and thorium to lead, are the result of a spontaneous disintegration of the atoms, more correctly of the nuclei, this disintegration being accompanied by the emission of α particles, β particles, and γ-rays. We thus have direct evidence that the atomic nuclei of the radioactive elements, at least, and, presumably, also of the other elements, contain α particles and electrons, perhaps also protons, all held together in equilibrium by some kind of mechanism or forces of which we have no knowledge.

We can make guesses—they are guesses only—as to the number of α particles, protons (call them "η particles"), and electrons ("β particles") which the radioactive nuclei may have. For example, uranium has atomic number 92 and atomic mass 238. From the atomic mass, we may conclude that the uranium nucleus contains 59 α particles and 2 η particles ($238 = 4 \cdot 59 + 2$). If so, the *total* positive charge on the nucleus must be ($2 \cdot 59 + 2$) or 120. But from the atomic number of uranium 92, we know that the net positive charge is +92. The uranium nucleus must, therefore, contain 28 electrons, and we may write symbolically the composition of the uranium nucleus as $\alpha_{59}\beta_{28}\eta_2$. Or, we might guess instead that the uranium nucleus contains 58 α particles and 6 η particles. The composition would then be $\alpha_{58}\beta_{30}\eta_6$. In the absence of experimental evidence, one guess is as good as another.

8. Gamma-ray Spectra.—Direct measurements of the wave lengths of some of the γ-rays have been made by use of the crystal grating. The wave length is so small in comparison, however, with the grating constants of available crystals that only the longer wave lengths can be measured in this way. Consequently, an indirect method has been developed based on the magnetic spectrum either of the secondary β-rays (photoelectrons) produced by γ-rays or, later, of the primary β-rays themselves.

The method employed by Ellis[1] has been followed, with modification, by subsequent investigators. The principle of the

[1] *Proc. Roy. Soc.* (London), vol. 99, p. 261 (1921).

method is identical with that used by Robinson (p. 515) in his investigation of the photoelectrons produced by X-rays. In Robinson's work, X-rays of known frequency caused the emission from various energy levels within the atom, of photoelectrons. By measuring by the so-called "magnetic spectrograph," the energies with which the various groups of electrons leave the atom, Robinson was able to compute the energy values of the levels from which they (the photoelectrons) originate. The procedure is reversed in the experiments of Ellis. Knowing the energy levels from which the photoelectrons emitted by γ-rays come, and the energies of these electrons as they leave the atom, the energy ($h\nu$) of the rays can be determined. In Ellis' experiments the source of the secondary rays was placed at W (Fig. 168) near a lead block B. W was a small glass tube 1 cm. long and 0.7 mm. in diameter, the inside walls of which were coated with a deposit of radium C which served as a source of the γ-rays under study. Around W was wrapped a foil of the metal M—Pb, Pt, W, etc.—which was to serve as the source of the secondary β-rays. The γ-rays passing out through the walls of the tube excite secondary β-rays, or photoelectrons, in the metal foil. The whole apparatus is placed in a magnetic field (and, of course, in a highly evacuated enclosure). The photoelectrons pass, in circular paths, through the wide slit S and are "focused" onto the photographic plate PP at L. On developing the plate, a number of "lines" are found corresponding to various electron energies which can be determined by knowing the magnetic field and the diameter LW of the circular paths.

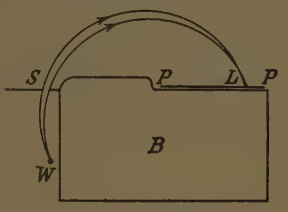


FIG. 168.—The β-ray spectrograph of Ellis.

The following data (Table III) taken from Ellis' paper will serve to illustrate the method of analyzing the results: For any given metal M there was observed a number of lines on the plate of which three were more intense. These same three appeared on the plate for each element but were shifted in position in such a direction as to indicate that the corresponding photoelectrons had *less* energy the *greater* the atomic number of M. This is shown in the upper part of Table III, in which the energies of the photoelectrons are expressed in equivalent volts.[1] Ellis concluded

[1] This is the potential difference in volts through which the electron would have to fall to give it the observed energy.

from a study of the data that these electrons were expelled from the K levels of the respective atoms by three different γ-ray frequencies. Applying Einstein's photoelectric equation

$$h\nu = E_k + W_K$$

where E_k is the observed kinetic energy of the photoelectron and W_K is the energy required to remove the electron from the K level of the atom M, one obtains at once the energy $h\nu$ of the three incident γ-rays Data from each metal M is found in this way to give the *same* group of three γ-rays, as the lower half of Table III shows. These then are three *lines* in the γ-ray spectrum of radium C, the respective wave lengths of which are 0.0518, 0.0425, and 0.0355 Ångström. In a similar way, energy values of many other lines in γ-ray spectra have been measured.

TABLE III.—DETERMINATION OF THE WAVE LENGTH OF γ-RAYS FROM THE ENERGY OF SECONDARY β RAYS (ELLIS)

Emittor——→	Tungsten 74	Platinum 78	Lead 82	Uranium 92		
Secondary β-ray energies in equivalent volts times 10^{-5}	1.66 2.20 2.76	1.58 2.12 2.69	1.49 2.03 2.60	1.22 1.74 2.31		
E_K of emittor——→	0.693	0.782	0.891	1.178	Mean energy	λ, Ångströms
Energy ($h\nu$) of γ-rays in equivalent volts times 10^{-5}	2.35 2.89 3.46	2.36 2.91 3.46	2.38 2.92 3.49	2.40 2.92 3.48	2.37 2.90 3.47	0.0518 0.0425 0.0355

Investigations of the *primary* β-rays emitted by radioactive bodies showed that the energies of these rays are in accord with the hypothesis that some of them are, in reality, photoelectrons coming from one or the other of the levels in the extranuclear structure of the radioactive atom itself as a result of the photoelectric action of the γ-ray as it passes from the nucleus where it originates out through the extranuclear structure. Consequently, in later work, the secondary metal radiator M is dispensed with and the source W (Fig. 168) is a fine wire coated with the radioactive deposit under study.[1]

[1] ELLIS and SKINNER: *Proc. Roy. Soc.* (London), vol. 105, p. 60 (1924).

9. Nuclear Energy Levels.—The measurements by Ellis and Skinner[1] of the γ-ray spectrum of radium B and C, and by Black[2] of the γ-ray spectrum of thorium products have yielded sufficient data so that it has been possible to postulate a system of energy levels in the nucleus, transitions between which give rise to γ-ray lines in exactly the same way that X-ray lines originate in transitions between levels in the extranuclear structure of the atom. The wave lengths and energy values (in equivalent volts) of some of the lines in the γ-ray spectrum of radium B, together with the "name" of the line, are shown in the first three columns of Table IV.

Following a procedure commonly applied to other spectral regions, Ellis and Skinner found it possible to postulate a series of *seven* energy levels A, B, C . . . transitions among which give rise to the *fourteen* lines given in Table IV, assuming the applicability of the ordinary quantum principles of the origin of spectral lines. The interlevel transitions giving rise to the several lines are given in column four, and an energy-level diagram is shown in Fig. 169. Tables V and VI give similar data

TABLE IV.—SOME LINES IN THE γ-RAY SPECTRUM OF RADIUM B AND THE ENERGY LEVELS IN THE RADIUM B NUCLEUS (ELLIS AND SKINNER)

Line	Wave length, Ångströms	Energy, volts times 10^{-5}	Origin	Proposed energy levels in the radium B nucleus, volts times 10^{-5}
C_2*	1.37	0.090	$B \rightarrow C$	$A = 0$
C_1	0.230	0.537	$A \rightarrow B$	$B = 0.537$
C_5*	0.196	0.629	$A \rightarrow C$	$C = 0.625$
C_3*	0.115	1.073	$E \rightarrow F$	$D = 2.572$
C_4*	0.098	1.250	$F \rightarrow G$	$E = 2.942$
E_1	0.0625	1.947	$C \rightarrow D$	$F = 4.048$
E_2	0.0616	2.035	$B \rightarrow D$	$G = 5.31$
E_3	0.0513	2.404	$B \rightarrow E$	
E_4	0.0480	2.572	$A \rightarrow$ B	
E_5	0.0451	2.733	$D \rightarrow G$	
E_6	0.0419	2.942	$A \rightarrow E$	
E_9	0.0351	3.511	$B \rightarrow F$	
E_{16}	0.0263	4.684	$C \rightarrow G$	
E_{17}	0.0257	4.800	$B \rightarrow G$	

* Measured by Rutherford and Andrade by crystal reflection.

[1] *Proc. Roy. Soc.* (London), vol. 105, pp. 165, 185 (1924).

[2] *Proc. Roy. Soc.* (London), vol. 106, p. 632 (1924); vol. 109, p. 166 (1925).

obtained by Black for two members of the thorium series. It may, or may not, be significant that no lines corresponding to certain of the (mathematically possible) transitions were found.

While much remains yet to be done in securing and in interpreting data on the γ-ray spectra of the radioactive elements, when one considers the difficulty of the measurements it is a

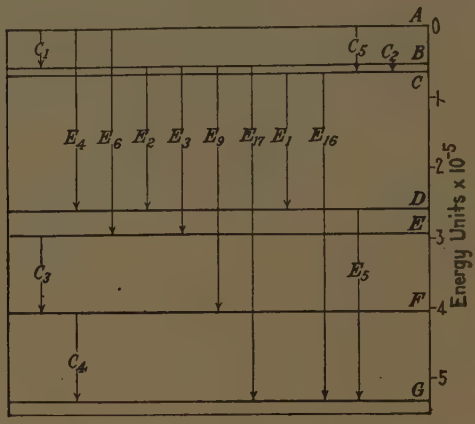


FIG. 169.—Energy-level diagram for the radium *B* nucleus, showing the origin of the γ rays (*Ellis and Skinner*).

scientific achievement of the first magnitude to have isolated and measured with acceptable precision the various γ-ray lines.[1]

TABLE V.—THE γ-RAY SPECTRUM OF MESOTHORIUM (BLACK, *loc. cit.*)

Line number	Wave length, Ångströms	Energy, volts times 10^{-5}	Origin	Proposed levels, volts times 10^{-5}
1	0.213	0.578	$A \rightarrow B$	$A = 0$
2	0.0955	1.291	$B \rightarrow C$	$B = 0.58$
3	0.0671	1.838	$A \rightarrow C$	$C = 1.84$
5	0.0365	3.38	$C \rightarrow D$	$D = 5.22$
6	0.0267	4.62	$B \rightarrow D$	$E = 9.72$
7	0.0135	9.14	$B \rightarrow E$	
8	0.0127	9.69	$A \rightarrow E$	

[1] The bulletin by Kovarik and McKeehan (*loc. cit.*, p. 551) gives an excellent account of measurements of radioactive phenomena and their interpretation up to 1925. Extensive tables are given showing data on α-, β-, and γ-rays.

TABLE VI.—THE γ-RAY SPECTRUM OF THORIUM D (BLACK, *loc. cit.*)

Line number	Wave length, Ångströms	Energy, volts times 10^{-6}
1	0.279	0.41
2	0.0791	1.45
3	0.0543	2.11
4	0.0491	2.33
5	0.0452	2.53
6	0.0442	2.59
7	0.0510	2.79
8	0.0393	2.91
9	0.0221	5.17
10	0.0171	6.58

10. The Structure of the Nuclei of the Radioactive Elements.—A mechanism capable of emitting α-rays, β-rays, and a whole spectrum of monochromatic γ-rays must possess a well-ordered, though probably very complex, structure. What type of structure does the existing data on radioactivity suggest? Perhaps it would be better not to attempt to form a "picture" of nuclear structure and processes. Nevertheless, the whole history of physics shows that "pictures," models, and analogies have played an indispensable part in the growth and development of all branches of physical theory. Most of us can think better in terms of models and geometrical relations.

Rutherford has attacked this problem[1] and has proposed a type of structure for the nucleus which in a rough way is analogous to the structure proposed by Bohr for the extranuclear part of the atom. The problem of *nuclear* structure is somewhat more complex than that of the extranuclear structure, since the latter contains only electrons while the former contains α particles, electrons, and, perhaps, protons.

Rutherford advances the suggestion that the nuclear structure of the radioactive elements comprises a central core, the radius of which is less than 1×10^{-12} cm., around which out to a distance of the order of 1.5×10^{-12} cm. from the center are found electrons. From 1.5×10^{-12} cm. to 6×10^{-12} cm. is a "shell" occupied by electrically neutral satellites in orbital rotation about the core. These satellites are helium-like structures consisting

[1] *Phil. Mag.*, vol. 4, p. 580 (September, 1927).

of an α particle to which are attached 2 electrons. Under the action of the strong electric field of the nucleus, the satellites become "polarized" in somewhat the same way as a neutral conductor becomes polarized by and is therefore attracted toward a charged body, and it is this force of attraction which holds the satellite in its orbit. A given configuration of the entire system corresponds to one of the energy levels, or states, suggested by Ellis and Skinner.

As a result of some kind of nuclear catastrophy, the equilibrium is disturbed and the positive part of the satellite, *i.e.*, the α particle, under the influence of repulsive forces, is projected from the structure with high velocity and the 2 electrons are pulled in toward the core around which they then circulate with a velocity "close to that of light." Occasionally one of these electrons is hurled from the system (how?) and becomes a high-speed β particle. As a result of this disturbance to the equilibrium of the system, the structure settles "down" to a new state, thereby emitting a γ-ray, the quantum energy of which is equal to the difference in the energy of the two states. This γ-ray in passing out through the extranuclear structure acts photoelectrically on the electrons, causing the expulsion of the lower-speed β particles such as those measured by Ellis and Skinner in the β-ray emission from radioactive substances.

This *picture* is not so significant as is the fact that sufficient data has been accumulated from a study of radioactive phenomena to make it possible to postulate a structure for the nuclei of atoms and to visualize thereby some of the processes which take place in the disintegration of atoms. What next? At the beginning of the century, there was a vague impression that the atom consists of electrical charges. We saw that Thomson's picture gave way, before experimental evidence, to the Rutherford-Bohr type of atom in which the *nucleus* was thought of as a *point* charge, just as the atom itself in the early chemical theories played the part of a *point mass*. Now, the nucleus itself succumbs to analysis, protons and electrons playing the part of *point* charges in the proposed structure. Will these, in their turn, yield to analysis and be assigned a structure? Or have we reached the end of the series?

Physics of today seems quite secure, in spite of the chasm between classical theory and quantum theory, but perhaps some day some Copernicus will appear who will completely overturn

our present exceedingly complex structure of physical theories and concepts and show us a beautiful simplicity in the laws of nature. If physics continues to grow at the present geometrically increasing rate, the physicist of a half-century hence will welcome such a revolution with open arms.

APPENDIX I(*a*)

ATOMIC NUMBERS AND ATOMIC[1] WEIGHTS

Number	Symbol	Name	Atomic weight[1]	Isotopes[2]
		First period		
1	H	Hydrogen	1.0077	1.0077
2	He	Helium	4.00	4.0
		Second period		
3	Li	Lithium	6.939	7, 6
4	Be / Gl[3]	Beryllium / Glucinium	9.02	9
5	B	Boron	10.82	11, 10
6	C	Carbon	12.000	12
7	N	Nitrogen	14.008	14
8	O	Oxygen	16.000	16
9	F	Fluorine	19.00	19
10	Ne	Neon	20,2	20, 22
		Third period		
11	Na	Sodium	22.997	23
12	Mg	Magnesium	24.32	24, 25, 26
13	Al	Aluminum	26.96	27
14	Si	Silicon	28.06	28, 29, 30
15	P	Phosphorus	31.024	31
16	S	Sulphur	32.065	32, 34, 33
17	Cl	Chlorine	35.458	35, 37
18	A	Argon	39.91	40, 36
		Fourth period		
19	K	Potassium	39.095	39, 41
20	Ca	Calcium	40.07	40, 44
21	Sc	Scandium	45.10	45
22	Ti	Titanium	47.9	48
23	V	Vanadium	50.96	51
24	Cr	Chromium	52.01	52
25	Mn	Manganese	54.93	55
26	Fe	Iron	55.84	56, 54
27	Co	Cobalt	58.97	59

ATOMIC NUMBERS AND ATOMIC WEIGHTS (*Continued*)

Number	Symbol	Name	Atomic weight[1]	Isotopes[2]
		Fourth period (continued)		
28	Ni	Nickel	58.69	58, 60
29	Cu	Copper	63.57	63, 65
30	Zn	Zinc	65.38	64, 66, 68, 70
31	Ga	Gallium	69.72	69, 71
32	Ge	Germanium	72.38	74, 72, 70
33	As	Arsenic	74.96	75
34	Se	Selenium	79.2	80, 78, 76, 82, 77, 74
35	Br	Bromine	79.916	79, 81
36	Kr	Krypton	82.9	84, 86, 82, 83, 80, 78, 81
		Fifth period		
37	Rb	Rubidium	85.44	85, 87
38	Sr	Strontium	87.62	88, 86
39	Y	Yttrium	89.0	89
40	Zr	Zirconium	91	90, 94, 92
41	Nb Cb	Niobium Columbium	93.1	
42	Mo	Molybdenum	96.0	
43	Ma	Masurium	97.5–98.8*	
44	Ru	Ruthenium	101.7	
45	Rh	Rhodium	102.91	
46	Pa	Palladium	106.7	
47	Ag	Silver	107.880	107, 109
48	Cd	Cadmium	112.41	110, 111, 112, 113, 114, 116
49	In	Indium	114.8	115
50	Sn	Tin	118.70	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
51	Sb	Antimony	121.77	121, 123
52	Te	Tellurium	127.5	128, 130, 126
53	I	Iodine	126.932	127
54	Xe	Xenon	130.2	129, 132, 131, 134, 136, 128, 130, 126, 124
		Sixth period		
55	Cs	Cesium	132.81	133
56	Ba	Barium	137.37	138, (136), (137)

ATOMIC NUMBERS AND ATOMIC WEIGHTS (*Continued*)

Number	Symbol	Name	Atomic weight[1]	Isotopes[2]
		Sixth period (continued)		
57	La	Lanthanum	138.91	139
58	Ce	Cerium	140.25	140, 142
59	Pr	Praseodimium	140.92	141
60	Nd	Neodymium	144.27	142, 144, 146, 145
61	Il	Illinium	146.0*	
62	Sm / Sa	Samarium	150.43	
63	Eu	Europium	152.0	
64	Gd	Gadolinium	157.26	
65	Tb	Terbium	159.2	
66	Ds / Dy	Dysprosium	162.52	
67	Ho	Holmium	163.4	
68	Er	Erbium	167.7	
69	Tm / Tu	Thulium	169.4	
70	Yb	Ytterbium	173.6	
71	Lu / Cp	Lutecium / Cassiopeim	175.0	
72	Hf	Hafnium	178.6	
73	Ta	Tantalum	181.5	
74	W	Tungsten	184.0	
75	Re	Rhenium	187.4*	
76	Os	Osmium	190.8	
77	Ir	Iridium	193.1	
78	Pt	Platinum	195.23	
79	Au	Gold	197.2	
80	Hg	Mercury	200.61	202, 200, 199, 198, 201, 204 196
81	Tl	Thallium	204.4	
82	Pb	Lead	207.20	206, 207, 208, (209), (203,) (204), (205),
83	Bi	Bismuth	209.00	209
84	Po	Polonium	210(?)	
85	?	?	212*	
86	Rn / Em / Nt	Radon / Ra-emanation / Niton	222	
		Seventh period		
87	?	?	223*	
88	Ra	Radium	225.95	
89	Ac	Actinium	229*	

ATOMIC NUMBERS AND ATOMIC WEIGHTS (*Continued*)

Number	Symbol	Name	Atomic weight[1]	Isotopes[2]
		Seventh period (continued)		
90	Th	Thorium	232.15	
91	Pa	Protoactinium	?	
	UX_2	Uranium X_2	234*	
92	U	Uranium	238.17	

[1] From International Critical Tables, except those marked *.
[2] That is, mass numbers of constituent atoms, where known.
[3] Alternative names and symbols are given in smaller type.
* Washburn, E. W., *Jour. Am. Chem. Soc.*, vol. 48, p. 2351 (1926). (Estimated by a graphical method.)

APPENDIX I(*b*)

The Periodic Table, Giving Atomic Numbers and Isotopes

Periods	I	II	III	IV	V	VI	VII	VIII
I	**1** *1* H 1.0077							**2** *2* He 4
II	**3** *1* Li 7, 6	**4** *2* Be 9	**5** *3* B 11. 10	**6** *4* C 12	**7** *5* N 14	**8** *6* O 16	**9** *7* F 19	**10** *8* Ne 20, 22
III	**11** *1* Na 23	**12** *2* Mg 24,25,26,28	**13** *3* Al 27	**14** *4* Si 28, 29, 30	**15** *5* P 31	**16** *6* S 32, 34, 33	**17** *7* Cl 35, 37	**18** *8* Ar 40, 36
IV	**19** *1* K 39, 41	**20** *2* Ca 40, 44	**21** *3* Sc 45	**22** *4* Ti 48	**23** *5* V 51	**24** *6* Cr 52	**25** *7* Mn 55	**26** *8* Fe 56, 54 · **27** *9* Co 59 · **28** *10* Ni 58, 60
	29 *11* Cu 63, 65	**30** *12* Zn 64,66,68,70	**31** *13* Ga 69, 71	**32** *14* Ge 74, 72, 70	**33** *15* As 75	**34** *16* Se (a)	**35** *17* Br 79, 81	**36** *18* Kr (b)
V	**37** *1* Rb 85, 87	**38** *2* Sr 88, 86	**39** *3* Yt 89	**40** *4* Zr 90, 94, 92	**41** *5* Cb	**42** *6* Mo	**43** *7* Ma	**44** *8* Ru · **45** *9* Rh · **46** *10* Pd
	47 *11* Ag 107, 109	**48** *12* Cd (c)	**49** *13* In 115	**50** *14* Sn (d)	**51** *15* Sb 121, 123	**52** *16* Te 128,130,126	**53** *17* I 127	**54** *18* Xe (e)
VI	**55** *1* Cs 133,(?)	**56** *2* Ba 138, 136	**57–71** *	**72** *18* Hf	**73** *19* Ta	**74** *20* W	**75** *21* Re	**76** *22* Os · **77** *23* Ir · **78** *24* Pt
	79 *25* Au	**80** *26* Hg (f)	**81** *27* Tl	**82** *28* Pb	**83** *29* Bi 209	**84** *30* Po	**85** *31* ?	**86** *32* Nt
VII	**87** *1* ?	**88** *2* Ra	**89** *3* Ac	**90** *4* Th	**91** *5* Pa	**92** *6* U		

(a) 80, 78, 76, 82, 77, 74
(b) 84, 86, 82, 83, 80, 78, 79, 81
(c) 110, 111, 112, 113, 114, 116
(d) 120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
(e) 129, 132, 131, 134, 136, 128, 130, 126, 124
(f) 202, 200, 199, 198, 201, 204

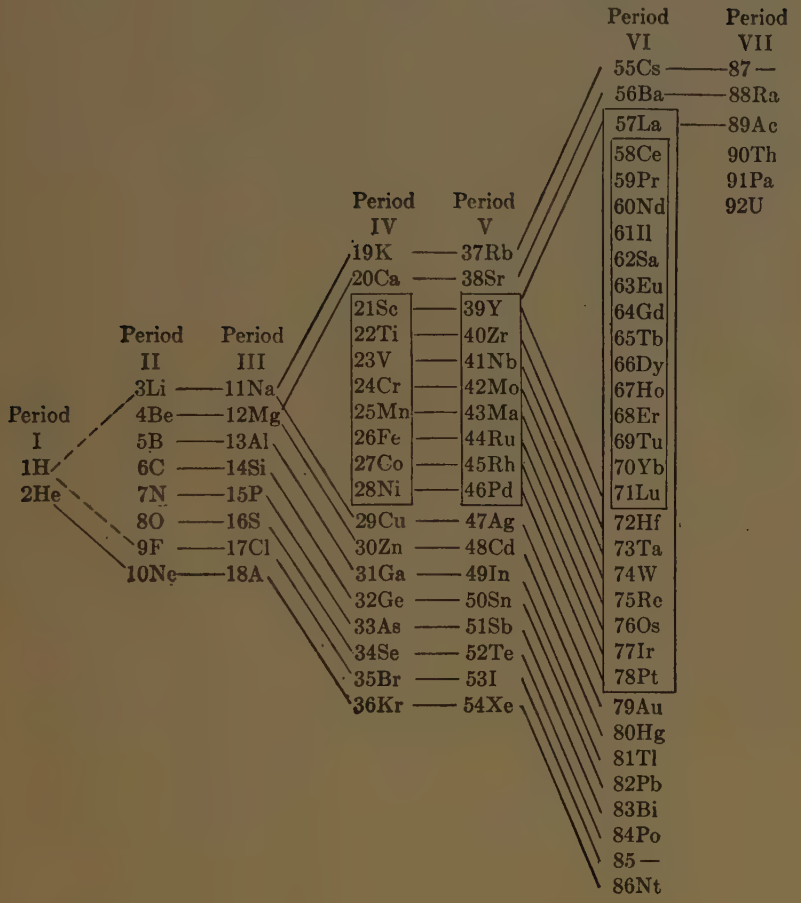
* *Rare Earths*

57 La	**61** Il	**65** Tb	**69** Tu
58 Ce	**62** Sa	**66** Dy	**70** Yb
59 Pr	**63** Eu	**67** Ho	**71** Lu
60 Nd	**64** Gd	**68** Er	

Explanation of the Table.—The Roman numerals in the top row designate the "columns" of the periodic table. The Roman numerals at the left give the several "periods" according to Bohr's arrangement (Appendix I(*c*)), and the italic numerals in the upper right-hand corners of the several spaces give the ordinal numbers of the elements in these periods. Atomic numbers are indicated by boldface type in the upper left-hand corners. Isotopes are given by the numbers at the bottoms of the spaces.

APPENDIX I(*c*)

Bohr's Periodic Table of the Elements



APPENDIX II

Arrangement of Electrons in Orbits According to Foote[1]

Period	Element	*	K	L_I L_{II} L_{III}	M_I M_{II} M_{III} M_{IV} M_V	N_I N_{II} N_{III} N_{IV} N_V N_{VI} N_{VII}	O_I O_{II} O_{III} O_{IV} O_V	P_I P_{II} P_{III} P_{IV}	Q_I
		n	1	2	3	4	5	6	7
		k	1	1 2 2	1 2 2 3 3	1 2 2 3 3 4 4	1 2 2 3 3 4	1 2 2 3	1
		j	1	1 1 2	1 1 2 2 3	1 1 2 2 3 3 4	1 1 2 2 3 3	1 1 2 2	1
I	1 H	1							
	2 He	2							
II	3 Li	2	1						
	4 Be	2	2						
	5 B	2	2 1						
	6 C	2	2 2						
	7 N	2	2 2 1						
	8 O	2	2 2 2						
	9 F	2	2 2 3						
	10 Ne	2	2 2 4						
III	11 Na	2	2 2 4	1					
	12 Mg	2	2 2 4	2					
	13 Al	2	2 2 4	2 1					
	14 Si	2	2 2 4	2 2					
	15 P	2	2 2 4	2 2 1					
	16 S	2	2 2 4	2 2 2					
	17 Cl	2	2 2 4	2 2 3					
	18 A	2	2 2 4	2 2 4					
IV	19 K	2	2 2 4	2 2 4		1			
	20 Ca	2	2 2 4	2 2 4		2			
	21 Sc	2	2 2 4	2 2 4 1		2			
	22 Ti	2	2 2 4	2 2 4 2		2			
	23 V	2	2 2 4	2 2 4 3		2			
	24 Cr	2	2 2 4	2 2 4 4 1		1			
	25 Mn	2	2 2 4	2 2 4 4 1		2			
	26 Fe	2	2 2 4	2 2 4 4 2		2			
	27 Co	2	2 2 4	2 2 4 4 3		2			
	28 Ni	2	2 2 4	2 2 4 4 4		2			
	29 Cu	2	2 2 4	2 2 4 4 6		1			
	30 Zn	2	2 2 4	2 2 4 4 6		2			

	31 Ga	2	2	2	4	2	2	4	4	6	2	1													
	32 Ge	2	2	2	4	2	2	4	4	6	2	2													
	33 As	2	2	2	4	2	2	4	4	6	2	2	1												
	34 Se	2	2	2	4	2	2	4	4	6	2	2	2												
	35 Br	2	2	2	4	2	2	4	4	6	2	2	3												
	36 Kr	2	2	2	4	2	2	4	4	6	2	2	4												
V	37 Rb	2	2	2	4	2	2	4	4	6	2	2	4				1								
	38 Sr	2	2	2	4	2	2	4	4	6	2	2	4				2								
	39 Y	2	2	2	4	2	2	4	4	6	2	2	4	1			2								
	40 Zr	2	2	2	4	2	2	4	4	6	2	2	4	2			2								
	41 Cb	2	2	2	4	2	2	4	4	6	2	2	4	4			1								
	42 Mo	2	2	2	4	2	2	4	4	6	2	2	4	4	1		1								
	43 Ma	2	2	2	4	2	2	4	4	6	2	2	4	4	2		1								
	44 Ru	2	2	2	4	2	2	4	4	6	2	2	4	4	3		1								
	45 Rh	2	2	2	4	2	2	4	4	6	2	2	4	4	4		1								
	46 Pd	2	2	2	4	2	2	4	4	6	2	2	4	4	6										
	47 Ag	2	2	2	4	2	2	4	4	6	2	2	4	4	6		1								
	48 Cd	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2								
	49 In	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	1							
	50 Sn	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2							
	51 Sb	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	1						
	52 Te	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	2						
	53 I	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	3						
	54 Xe	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	4						
VI	55 Cs	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	4						1
	56 Ba	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	4						2
	57 La	2	2	2	4	2	2	4	4	6	2	2	4	4	6		2	2	4	1					2
	58 Ce	2	2	2	4	2	2	4	4	6	2	2	4	4	6	1	2	2	4	1					2
	59 Pr	2	2	2	4	2	2	4	4	6	2	2	4	4	6	2	2	2	4	1					2
	60 Nd	2	2	2	4	2	2	4	4	6	2	2	4	4	6	3	2	2	4	1					2
	61 Il	2	2	2	4	2	2	4	4	6	2	2	4	4	6	4	2	2	4	1					2
	62 Sm	2	2	2	4	2	2	4	4	6	2	2	4	4	6	5	2	2	4	1					2
	63 Eu	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	2	2	4	1					2
	64 Gd	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	1	2	2	4	1				2
	65 Tb	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	2	2	2	4	1				2
	66 Dy	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	3	2	2	4	1				2
	67 Ho	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	4	2	2	4	1				2
	68 Er	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	5	2	2	4	1				2
	69 Tm	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	6	2	2	4	1				2
	70 Yb	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	7	2	2	4	1				2
	71 Lu	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	8	2	2	4	1				2
	72 Hf	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	8	2	2	4	2				2
	73 Ta	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	8	2	2	4	3				2
	74 W	2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	8	2	2	4	4				2

[1] *Trans. Am. Inst. Min. Metal. Eng.*, vol. LXXIII, p. 628, February (1926).

ARRANGEMENTS OF ELECTRONS IN ORBITS ACCORDING TO FOOTE (*Continued*)

Period	Element	*	K	L_I L_{II} L_{III}	M_I M_{II} M_{III} M_{IV} M_V	N_I N_{II} N_{III} N_{IV} N_V N_{VI} N_{VII}	O_I O_{II} O_{III} O_{IV} O_V	P_I P_{II} P_{III} P_{IV}	Q_I
		n	1	2	3	4	5	6	7
		k	1	1 2 2	1 2 2 3 3	1 2 2 3 3 4 4	1 2 2 3 3 4	1 2 2 3	1
		j	1	1 1 2	1 1 2 2 3	1 1 2 2 3 3 4	1 1 2 2 3 3	1 1 2 2	1
VI	75 Re[1]		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 1	2	
	76 Os[1]		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 2	2	
	77 Ir[1]		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 3	2	
	78 Pt[1]		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 4	2	
	79 Au		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	1	
	80 Hg		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2	
	81 Tl		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 1	
	82 Pb		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2	
	83 Bi		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 1	
	84 Po		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 2	
	85 —		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 3	
	86 Rn		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4	
VII	87 —		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4	1
	88 Ra		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4	2
	89 Ac		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4 1	2
	90 Th		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4 2	2
	91 Pa		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4 1	2
	92 U		2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4 1	2

[1] Alternative arrangements are suggested by Foote for these elements.

*K, L, M . . . = X-ray levels.
n = total quantum number.
k = azimuthal quantum number.
j = inner quantum number.

APPENDIX III

Some Important Constants[1]

c	velocity of light	2.9986×10^{10} cm. sec.$^{-1}$
e	electronic charge	4.774×10^{-10} e.s.u.
e'	electronic charge	1.592×10^{-20} e.m.u.
m	electronic mass	8.999×10^{-28} grams
$\frac{e}{m}$		5.305×10^{17} e.s.u. gm.$^{-1}$
$\frac{e'}{m}$		1.769×10^{7} e.m.u. gm.$^{-1}$
h	Planck's constant	6.554×10^{-27} erg-second
F	the faraday	9.6500×10^{4} coulombs
R	gas constant	1.9869 calories deg.$^{-1}$-mole^{-1}
R	gas constant	8.315×10^{7} erg-deg.$^{-1}$-mole^{-1}
N_o	Avogadro's number	6.061×10^{23} mole^{-1}
k_o	Boltzmann's constant	1.372×10^{-16} erg-deg.$^{-1}$
m_H	mass of the hydrogen atom	1.663×10^{-24} grams
σ	Stefan's constant	5.709×10^{-5} erg-cm.$^{-2}$-sec.$^{-1}$deg^{-4}
W	Wien's displacement constant	0.2885 centimeter degrees
N_∞	Rydberg's wave number	1.0930×10^{5} cm.$^{-1}$
	Grating space of calcite	3.0288×10^{-8} cm.
	Wave length of red cadmium line	6438.4696×10^{-8} cm.

[1] From the International Critical Tables Vol. I. p. 18.

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